AMERICAN DYESTUFF REPORTER

"Circulated Everywhere Dyestuffs Are Used"

Published by Howes Publishing Company, 440 Fourth Avenue, New York

Devoted to the practical application of dyestuffs in all industries; especially to textile chemistry—the science and practice of scouring, bleaching, dyeing and finishing.

Volume XIX | AUGUST 4, 1930 | Number 13

Dyeing Rayon and Rayon Mixtures

By **E. M. MARGIS**

THE dyeing of rayon, either alone or in mixtures with other textiles, has become quite an essential part of the dyer's business. Those who have followed the market reports on dyestuffs during the past months have seen it frequently reported that rayon is the only branch of the textile industry that is actually holding its own, as far as consumption of dyestuffs for its dyeing and printing is concerned, in the difficult economic times through which we are passing. It is, therefore, evident that the average dyer today is much interested in rayon and in its correct dyeing.

It was inevitable that the dyeing of rayon should have appeared to be a simple matter, highly analogous to the dyeing of cotton or at least of mercerized cotton, at the first glance. There is no doubt that the dyeing of rayon is quite like that of cotton, but the dyer has learned from his own experience that rayon does not dye altogether like its parent fiber but has certain peculiarities of its own which require special treatment and consideration. We refer here to all the rayons with the exception of acetate rayon which is in a class all by itself, as far as tinctorial properties are concerned and cannot be considered here.

Dyers have often found irregularities in dyeing rayon, not to mention the troubles that arise in dyeing mixtures of rayons and cotton and silk. Rayon will dye irregularly at times. Thus in dyeing the yarn, some skeins will be found to dye more deeply than others, although apparently all the conditions are being maintained constantly. Then again when dyeing piece goods, irregularity in dyeing will be manifested at times by warp streaks and filling bars, these of varying width. Such bars will also be recognized in tubular knit goods. The important question is, what is the cause of these troubles and how can they be stopped?

The manufacturer of the rayon product has been blamed for these difficulties and disabilities. It is true enough that rayon is made by a highly complicated physical-chemical process or processes. There are many opportunities for irregularities in the composition and constitution of the rayon filament due to variations in the manufacturing conditions, in the ripening, the desulphurization of viscose rayon and the like. While in the early days of the rayon industry, the producer could well be blamed for these troubles, nevertheless, the efficiency of the modern rayon yarn manufacturer is so great that the user of the yarns can well be assured of their uniformity. One condition is still perhaps not completely overcome and that is the troubles that arise when yarns of different make are used together by the weaver. However, the weaver today has learned to use just one brand of yarn in weaving a certain order, and this is also true for the knitter. It therefore remains that if trouble is still encountered in the irregular dyeing of rayon the cause of the same must be looked for in the dyeing operation itself.

Before considering what the dyer can himself do to obtain level shades on rayon, one peculiar property of rayon, which may sometimes cause irregular dyeing in the piece, must also be mentioned. The rayon filament is very sensitive to moisture and to changes of the humidity of the air. It has often been claimed that the only really proper way in which to weave or knit rayon is in rooms which are insulated against the atmosphere and in which both the temperature and the humidity of the air are controlled. This is desirable but seldom possible for economic reasons. The variation in the elasticity and strength of the rayon caused by variation in the moisture content of the air may well cause irregularities in the state of the rayon filament during winding, reeling, knitting and weaving. This will also be manifested in streaky dyeing, which the dyer cannot help no matter how skillful he may be.

Before the dyer can be sure that the rayon, either alone or in mixtures, will dye in regular shades, he must be sure that the fabric or yarn is absolutely clean, free from oil, grease, dirt and other impurities. Rayon warps are sized. The yarns are oiled so that they may be properly used in weaving and knitting. Some processors may use linseed oil sizes and when the rayon warps are stored for some time, the linseed oil resinifies, just like it does in

paint and varnish. The removal of such hardened oils is quite a difficult matter as is also the removal of oiling preparations, which contain too much mineral oil, for the latter is insoluble and cannot be saponified. The scouring of rayon prior to its dyeing is therefore a very important operation in the dyeing of rayons. The use of hot soap solutions containing suitable fat solvents is best practice. The dyer must, however, be sure that he buys the right kind of fat solvent, one that is properly made and that does not contain substances which attack the rayon filament and reduce its strength. This is a very important point that must be remembered by the dyer in scouring rayon for the reason that rayon in the wet state is highly sensitive to the action of various chemicals. The use of a little soda in the bath is also advisable, although care should be taken to see that only a small amount is employed. This is particularly desirable when the warp size contains oils and substances that solidify and form resinous substances which are difficult to remove under ordinary conditions. The temperature of the bath is generally maintained at 158 to 175 degrees F.

Temperature

A word might well be said here regarding the importance of maintaining the correct temperature during the scouring as well as the dyeing process. Temperature is one of the most important factors in the chemical processing of any textile, not to mention rayon, and more important in the case of rayon than in any other, for the reason that rayon is a substance which is more sensitive to temperature than the other textiles. Too high temperatures in scouring rayon may well result in irreparable injury to the rayon filament. On the other the faulty control of the temperature during the dyeing process may impair the dyeing results. In the case of dyeing mixtures of rayon and cotton, the maintenance of the correct temperature is highly important, for this is one of the principal means available for controlling the adsorption of the dyestuff so that level shades are obtained both on the rayon and the cotton portions of the fabric.

Temperatures may be regulated by hand. This is of course possible. It is, however, not best practice, for too much reliance is put in this case upon the skill and perseverence of the operator. Good results have been obtained by using automatic regulating instruments. These are now made so accurately that they can control the temperature within a degree Fahrenheit. When a controller is used along with a recorder, which affords a complete picture of the dyeing or other operation by the medium of a curve traced on a chart recording the variation of temperature during the operation. The recorder also checks the regulator to show how well it is controlling the temperature. The use of these two instruments in the dyeing and other processes carried out in the dyeing plant affords important economies, and helps materially to conserve the high quality and properties of the rayon filament.

Another point which must be given careful consideration in level dyeing of rayon is the proper choice of dyestuff. In spite of the addition of all sorts of assistants to the dye liquor and the control of temperature, it is true that level results cannot be obtained with certain dyestuffs. As far as temperature regulation is concerned, the best results seem to have been obtained at temperatures as high as possible without injuring the filament. Another attempt to obtain level shades has been based on the use of substantive dyestuffs in an acid bath. However, this method is reported not to have given good results. The after-treatment of the dyed fabric or yarn to improve the levelness of the shade will give good results under certain conditions, but it is always accompanied by the disadvantage that the shade of the entire fabric is changed and this makes it difficult to match shades. Dyers do not look with favor on such a method.

Careful selection of the correct dyestuff will help materially. The manufacturers of dyestuffs have given much attention to this matter. This is basically an empirical matter, for the reason that one dyestuff of a group will act differently than another. There is no general law according which the dyestuffs can be correctly judged, as far as their level dyeing properties are concerned. There therefore remains the empirical method of testing each color to see what results are obtained from it. The unfortunate part about the entire matter is that the number of dyestuffs, that will give good results when used on rayons, is rather small, and it often happens that when such a dyestuff does dye rayon in level shades, it possesses the disadvantage of poor fastness to water and washing. This is actually the situation at the present time and must be accepted as such by the dyer. One point he should remember and that is that he should not by any means make a haphazard selection of dyestuffs in dyeing rayon or base his selection on the assumption that because the dyestuff gave good results in dyeing cotton, it is bound to give like results in dyeing rayon.

An interesting development, which is of importance to the dyer of rayon, is the result of work done to connect the level dyeing properties of the color with its other properties, such as constitution or colloidal characteristics. The work done by Whittaker in England is also highly significant. This investigator has developed the hypothesis that a dyestuff, which gives most level shades on viscose rayon, must possess maximum affinity for the filament at a temperature of 68 degrees F. The truth of the matter is that there are only a few dyestuffs which meet this stringent requirement, and the rule must not be interpreted too rigidly. Satisfactory dyestuffs are also those which will dye the rayon filament nearly as well at higher temperatures as at 68 degrees F.

It has been mentioned that the level dyeing colors are often found to be wanting in satisfactory fastness characteristics. The vat colors are known for their fastness and level shades have been obtained with these colors on rayon. The vat colors cannot be used on any other rayon besides cuprammonium and viscose rayons. These colors are of course used in an alkaline bath and when it happens, as it often does, that they give irregular shades, it is quite difficult, if not impossible, to correct the fault

by stripping or levelling-off. The additional chemical treatment, which this involves, practically ruins the rayon which after all is not well-treated by the alkali in the dye liquor in the first instance. It therefore follows that the only way to guard against irregular dyeing is to take the proper precautions in the actual dyeing process itself.

In the first place it must be borne in mind again that the use of dyestuffs rests on empirical grounds, and that one vat color should not be treated in the same manner as another. There may be certain standard directions which the dyer may follow, but it is best for him to consider the use of a particular dyestuff as a special case.

Care must be paid to the composition of the bath. It must be such that the dyestuff is completely dissolved in it and is also completely reduced. The correct amount of caustic soda and hydrosulphite must be used according to the directions furnished by the makers of the colors. In order that the dyestuffs may be completely dissolved in the bath, it is essential that it should be gradually added in the usual paste form through a sieve. It should be thoroughly stirred into the solution. It has been recommended that the vat solution, made up according to standard, should be passed through a sieve to remove any lumps of color that might be present in it. It is understandable that level shades could not possibly be obtained if the vat contained lumps of dyestuffs. Another detail that the dyer should bear in mind is that the temperatures, which are prescribed for dyeing with these vat colors by the manufacturers, must be strictly adhered to.

Dyeing With Vat Colors

The secret of level dyeing with vat colors is proper vatting. The temperature must be regulated, the salt properly proportioned and added in the proper portions. It has sometimes been found advantageous in dyeing light shades or in using colors which are known to dye level shades with difficulty only, to use a warm vat at the beginning but to finish the dyeing in the cold, or in a moderately warm vat. This can be done in the following manner: The bath of sodium hydroxide dyestuff and sodium hydrosulphite is prepared with half the quantity of warm water and then after the vatting is completed to fill the bath with the remainder of cold water. The goods are then entered in the usual manner and the temperature is gradually increased during the dyeing process, at the most an additional 18 to 36 degrees F.

The manner of the addition of salt is highly important in guarding against faulty levelling. The amount of salt added gives the dyer an opportunity of regulating the rate of adsorption of the color. The unfortunate part about this detail of the process is that the only way in which the affinity of the dyestuff in the vat can be judged is by the results obtained after oxidation of the color. It, therefore, requires considerable skill to obtain good results. It may be mentioned here that the addition of dyeing assistants and colloids are useful in controlling the rate of adsorption of the color and in aiding the dyer to obtain level shades. The importance of complete oxidation after dyeing is also worthy of mention. The dyer must be careful to see that all excess vat liquor has been squeezed out of the goods after they are taken from the vat and made ready for oxidation.

The dyer, who is called upon to dye mixtures of cotton and rayon, has experienced the condition that the rayon filament will adsorb the dyestuff much more rapidly than the cotton portion, with the result that if the fabric is allowed to remain in the dye bath long enough for the proper shade to be obtained on the cotton portion, the rayon portion will appear darker than the latter. If he takes the fabric out of the bath too quickly, then the cotton portion is still dyed in lighter shade than the rayon portion. Within recent times a process for mercerizing the cotton in the mixture of cotton and rayon has been developed and this undoubtedly changes the condition of the cotton fiber so that its rate of adsorption of the dyestuff is more closely that of the rayon filament. There is also no question that the dyeing is rendered easier by this process and, furthermore, that the appearance of the fabric is much improved.

There are, however, means of obtaining good level shades both on the cotton and the rayon portions of the mixed fabric without the need of mercerizing the cotton. This depends definitely on the manner in which the dyeing process is carried out and on the proper selection of the dyestuffs used.

Thus, in one process, wherein substantive colors are used, the dye bath contains approximately five per cent of castile soap. The dyeing is conducted for half an hour at the boiling temperature and the goods are allowed to remain in the bath for another half an hour after the steam has been shut off. Certain dyestuffs are suitable for this process and amongst them may be mentioned Sirius Yellow 5G, Benzo Pure Gold FF, Dianil Fast Orange O, Benzo Fast Scarlet 5BS, Chloramin Red 8BS, Sirius Violet BL, Sirius Blue B, Sirius Brown G, Dianil Brown S, Black V, Diazo Brilliant Orange GR extra, etc.

In another process the dye bath contains as heretofore approximately five per cent of castile soap and also ten per cent of Glauber's salt. The dyeing of the fabric is carried out for half an hour at the boiling temperature and then the goods are left in the liquor for another half an hour after the steam is shut off. Some dyestuffs, which are suitable for use by this process, are Dianil Yellow R, Diamin Scarlet B, Dianil Light Red 8BW, Sirius Green BL, Dianil Brown SGR, Benzo Light Brown RL, Artificial Silk Black A, Zambesi Black V, and the like.

In the third process of dyeing mixtures of cotton and viscose rayon with the aid of substantive dyestuffs, the dye bath contains five per cent of a sulphonated castor oil preparation and twenty per cent of Glauber's salt. The dyeing is carried out for a period of one hour at a temperature of approximately 120 degrees F. A number of substantive dyestuffs are specially suitable for use in this process and amongst them may be mentioned the following: Benzo Pure Yellow FF, Chrysophenin G, Benzo Light Orange G, Dianil Fast Orange O, Columbia Fast Scarlet S5B, Benzo Fast Scarlet 6BSS, Chloramin Violet

FFB, Benzo Copper Blue BB (this dyestuff can be used direct and after the material has first been treated with a copper salt), Benzo Azurine G, Diamin Green B, Dianil Brown S, Diamin Fast Black CB, Dianil Orange RR, Pure Blue GL, Diazo Light Green GF, Diazo Brown B, Zambesi Black V, Diaminogen B (to obtain grays), Diazo Brilliant Orange 5G, extra, etc.

It has also been found possible to obtain level shades on mixtures containing both rayon and cotton by using direct colors, and by altering the conditions of the process of dyeing so that the rate of absorption of the dyestuff by the cotton and by the rayon portions of the fabric are separately controlled at different stages of the process. It has been found that when direct dyestuffs are employed in the dyeing of cotton and viscose rayon mixtures at comparatively low temperatures in dye baths which contain only a small proportion of salt, there is a far better chance of obtaining a level shade than when the temperature of dyeing is high, and the proportion of Glauber's salt in the bath large. It has been found that the best results are obtained in a dye bath which contains from five to fifteen per cent of Glauber's salt. The ratio of liquor to fabric is as 30 to one. The temperature at the start of the dyeing process is 85 degrees F. and it is then gradually increased to between 120 to 140 degrees F.

Under these conditions deep shades are obtained on the mixture of cotton and viscose rayon, but only with a high consumption of dyestuff.

Some interesting observations have been made on the behavior of the textile in the mixture of cotton and viscose rayon with respect to the dyestuff and these have been substantiated by acyial experiment. When the temperature of dyeing is high, the affinity of the viscose filament for the dyestuff is increased. The conclusion is that the viscose filament must possess greater affinity for the highly dispersed phase than does cotton, for as the temperature of the dye bath increases the degree of dispersion of the dyestuff in the bath also increases.

On the other hand, when the degree of dispersion of the dyestuff is reduced even though the temperature remains high, the affinity of the dyestuff for the cotton portion of the mixed fabric must be increased.

The degree of dispersion of the dyestuff in the dye liquor can, of course, be regulated by the proportion of Glauber's salt added to it as well as by the temperature. When the proportion of Glauber's salt is increased, the degree of dispersion of the dyestuff is decreased and if the proportion is large enough the degree of dispersion becomes zero or the dyestuff is precipitated. It has been found from actual test that when the proportion of Glauber's salt in the dye liquor is increased to abnormal amounts, the affinity of the dyestuff for the rayon filament becomes very much less with the result that the cotton portion of the fabric is dyed in deeper shade than the rayon portion. It is possible to work out a theoretically perfect process whereby the dyeing of mixtures of cotton and viscose rayon can be controlled so that level shades are obtained, the proportion of Glauber's salt and the temperature being the two principal factors requiring regulation in addition, of course, to the selection of the proper dyestuff.

Many attempts have been made to dye mixtures of cuprammonium rayon and cotton in level shades and up to the present time it has been found desirable to use mercerized cotton in making the mixture if level shades are to be obtained. The cuprammonium filament possesses a very great affinity for the dyestuff, much greater than that of cotton and it appears to be almost impossible to obtain level shades on mixtures of these textiles. Mixtures of mercerized cotton and cuprammonium rayon are dyed readily in level shades by using a bath which does not contain any salt at all. The fabric is directly entered into the bath which at first has a temperature of 185 to 195 degrees F. and is permitted to dye for a short time at this temperature. Then the temperature of the bath is raised up to the boiling point and the dyeing is continued at this temperature for about twenty minutes. This process works well with the Diphenyl mark dyestuffs.

While the general problem of dyeing mixtures of rayon and cotton in level shades is quite a difficult one, it becomes even more difficult when the mixture is woven in the nature of a hat ribbon. The nature of the weave is what causes the added difficulty. In the rep weave in which the rayon filaments cover the cotton, it is highly desirable that the cotton should be dyed in deeper shade than the rayon under these conditions. Many experiments have been made in which the materials were preliminarily treated with one chemical or another. Then again various assistants and the like have been added to the dye liquor. While these variations in the dyeing process may produce some favorable results under the best conditions, they are generally of no avail. Here again it has been found that a careful selection of the dyestuff used is the most helpful procedure in attaining level shades as well as the adaptation of the dyeing process to the nature of the fabric being dyed, for it has been found that not every material can be dyed in the same manner.

The Bath

As far as the composition of the bath is concerned, it has been found best to include soap as well as Glauber's salt in it. The temperature of dyeing has been determined as most favorable at about 115 to 125 degrees F. Nevertheless, this process cannot always be used in dyeing ribbons for the reason that the proper penetration of the dyestuff into these fabrics often requires dyeing at the boiling temperature of the dye bath or close to the latter.

When light shades are required, best results are usually obtained by dyeing for half an hour at the boiling temperature in a bath which contains five per cent of castile soap. The temperature need not be quite as high as the boiling point in some cases. The fabric is allowed to remain in the dye liquor after the half-hour period is over with the steam shut off. The ad-

ditional time required in this stage of the dyeing process is also half an hour. There are a number of colors that can be advantageously used under these conditions, some of which are: Benzo Pure Yellow FF, Chrysophenin G, Sirius Yellow 5G, Dianil Fast Orange O, Sirius Scarlet B, Benzo Fast Scarlet 5BS, Sirius Red BB, Sirius Pink BB, Chloramin Red 8BS, Chloramin Violet FFB, Sirius Violet 3B, Sirius Brown G, Dianil Brown S, Sirius Blue B, Dianil Blue B.

These colors can be successfully used in the production of light and medium depth shades which are either moderately fast to light or very fast to light. It has been found in dyeing mixtures of mercerized cotton and viscose rayon in delicate shades that the viscose rayon portion of the fabric is colored in lighter shade than the cotton portion of the fabric. This is contrary to what happens in dyeing mixtures of these textiles in deeper shades.

It is understandable that the difficulties in obtaining level shades on mixtures of cotton and viscose rayon are much greater when the required shade is a deep one. Dyeing the mixture in a bath, which does not contain any salt, does not produce the desired results when the dark shades are required. It is necessary under these conditions to add Glauber's salt and generally from ten to twenty per cent of the salt is required. Such dyestuffs as Benzo Pure Yellow FF, Dianil Yellow R, Dianil Brown SGR, Dianil Fast Orange O, Chloramin Violet FFB and Artificial Silk Black G, have been found to give very good results when used in the afore-described manner.

When the mixture of rayon and cotton is being dyed in black, then it is advisable to use high proportions of the dyestuff, that is, with at least ten to twelve per cent of the dyestuff in the bath. This is the only way to be sure that the cotton portion of the fabric is properly dyed. When Artificial Silk Black G is used, it is claimed that there need be no fear regarding the bronzing of the shade. Dark green and dark blue shades on ribbon fabrics containing both viscose rayon and cotton can be obtained with the aid of Diamin Green B, Benzoazurin G, Benzo Chrome Black Blue B, Benzo Copper Blue BB and the like at a temperature of 125 degrees F., approximately, in a bath which contains twenty per cent of Glauber's salt and five per cent of castile soap. The dyeing is prolonged for one hour.

Adsorption and Its Action in Dyeing of Textile Fibers

An Explanation of a Little Understood Phenomenon

By **S. R. TROTMAN, M.A., F.I.C.**

THE phenomenon of "adsorption" plays a part in many textile processes; in fact, in its absence the scouring, bleaching and dyeing of textile materials would become very difficult, if not impossible. Like some other physical phenomena, it is not very easy to understand, and is often confused with the simpler manifestation of "absorption." Before considering the effect of adsorption in textile processes, the difference between it and absorption may be discussed briefly.

This difference is illustrated by the result obtained when one liquid is poured on to the surface of another which has a greater specific gravity and upon which the lighter liquid has no chemical action. Let us consider the case of alcohol and water—(Slater, Journ. Soc. Chem. Ind., 1925, 161). When alcohol is poured carefully on to the surface of water, it forms, at first, a layer which is separated sharply from the water beneath it. The molecules of both water and alcohol are in a state of constant motion and hence, at the junction of the two liquids, there is a tendency for them to become mixed. When there is nothing to hinder the excursions of the molecules, that is, when the surface between the two liquids does not resist penetration, a homogeneous mixture is gradually produced.

This uniform mixture of the molecules is termed "absorption," although, of course, other terms of description may be used, such as "miscibility" or "solubility." When a solid body absorbs a liquid the same intermingling of the molecules occurs, as is also the case when two solid substances such as metals form a homogeneous mixture.

Acetic Acid and Charcoal

Suppose now that when one liquid is poured on to the surface of another, the surface separating them completely resists penetration by the molecules of either. In

this case the molecules are deflected from it, or bounce off, directly they strike it and the two liquids remain unmixed. But if one of the liquids contained a dissolved substance the molecules of this might, in their attempts to penetrate the surface, become concentrated at the surface of the second liquid. This is known as "adsorption."

When a solid body such as charcoal is exposed to the action of an aqueous solution of acetic acid, it exercises some attractive force on the molecules of the acetic acid. The molecules of the acid, when they strike the charcoal, are held by this force and thus become, temporarily at any rate, a part of the solid substance. This is a typical example of adsorption, which may, therefore, be defined as the concentration of one substance at the surface separating it from another, producing a layer of increased concentration of only a few molecules in thickness. In the case of dilute solutions of acetic acid, practically all the acid may be removed from solution, but with more concentrated solutions, the quantity of acid retained by the charcoal increases less rapidly as the concentration of the solution increases.

Why the Action Is Not Chemical

It must be noted carefully that the removal of the acetic acid by charcoal is not due to chemical action, for the following reasons:

(1) Charcoal has no chemical affinity for acetic acid.

(2) It acts in the same way towards many other substances, such as dyestuffs or inert gases such as nitrogen.

(3) If a definite chemical compound were formed, the amount of acid taken up would be independent of its concentration.

(4) The action is reversible.

If charcoal be treated with a fairly concentrated solution of acetic acid, a definite quantity of the latter will be taken up. But if the charcoal be washed with a more dilute solution of acetic acid, some of the acid will be removed; if washed repeatedly with water, the whole of it can be recovered. For every concentration of acid there is a definite quantity which can be retained by the charcoal. The amount is expressed by the formula of Freundlich:

$$\frac{V}{N} = KC^{1}$$

where "V" is the amount of acid taken up; "C" the concentration of the liquid; "K" and "N" constants depending on the nature of the liquid and the solid.

As noted above, gases are adsorbed by solids in the same way as liquids. Thus, wool adsorbs sulphur dioxide and other gases, and silica-gel is used for the recovery of gases and organic vapours in the artificial silk industry because of its power of adsorption.

The amount of adsorption which can take place depends primarily, that is, excluding attractive forces, upon the number of molecules which strike the surface in the unit of time and their rate of movement. The number of molecules striking the surface is governed by the pressure in the case of a gas and the concentration in the case of a liquid. The rate of movement is determined by the temperature. These two factors act in opposite ways, the amount of adsorption varying directly with pressure of concentration and inversely with the temperature.

Although adsorption is in general a reversible process, this is not strictly true. If it were, dyeing and many other industrial operations which depend primarily upon adsorption would become impracticable. There are other factors besides those mentioned already which exercise an influence on the results. The chief of these are (1) surface tension; (2) electric charges; (3) chemical action. These can be dealt with briefly.

Since adsorption is due to a concentration of molecules at the surface of the adsorbent, it is natural that it should be exhibited chiefly by bodies with large surfaces. Colloids, such as wool, which consist of molecular complexes, are always good adsorbents. It has been shown that one gram of silica-gel has a surface area 5,000 sq. ft. A large surface area does not, however, of itself bring about adsorption. Gibbs showed that adsorption is connected with the surface tension between the liquid and solid, a substance being adsorbed only when it lowers the surface tension of the liquid and not when it increases it. Direct dyestuffs are adsorbed by cotton from their aqueous solutions because they lower the surface tension of the water, which is itself comparatively small. The surface tension of alcohol is much higher than that of water. If alcohol be added gradually to an aqueous solution of a direct dyestuff such as chrysophenine, the surface tension of the liquid will gradually increase until a point is reached when adsorption cannot take place. In the case of viscose, a comparatively small proportion of alcohol inhibits adsorption completely at ordinary atmospheric temperatures. The surface tension of the solid also affects adsorption, but its action is very difficult to investigate, and is constant for any particular solid.

Electric Charges

Many substances when dissolved in water are dissociated into ions charged with equal quantities of positive and negative electricity. If the adsorbent be charged also, it will naturally attract the ions which are charged oppositely and repel those having the same charge. This may either promote or retard adsorption, or prevent it from taking place. The effect of electric charges may be illustrated by the following example. When wool is heated in an aqueous solution of many acid dyestuffs containing sulphuric acid it shows no affinity for the color until a temperature of 140 deg. F. is reached. It has been shown by Haldane, Gee and Harrison (J. Soc. Dyers' Col., 1910, 484) that the wool is charged primarily with negative electricity. The acid dyestuff is dissociated into negatively charged RSO_3 ions and positively charged sodium ions.

The wool repels the similarly charged ions and no adsorption can take place. But when the temperature is raised to 140 deg. F., the charge on the wool becomes positive and now attracts the RSO_3 ions, thus making adsorption possible. Since hydrogen and hydroxyl ions

are always charged with positive and negative electricity respectively, the presence of acids or alkalies will often affect adsorption. Thus the presence of hydroxyl ions promotes the adsorption of direct dyestuffs by cotton and retards it in the case of wool, whilst hydrogen ions increase the adsorption of chlorine by wool. Salts which dissociate into positively and negatively charged ions may act in the same manner, those carrying an opposite charge to the adsorbent being taken up the more readily than or to the exclusion of the other.

Chemical action is undoubtedly the most important factor which influences adsorption, since, in many cases, it prevents an equilibrium of the reversible action from becoming established by continuously removing the adsorbed substance from the sphere of action. This is illustrated by the dyeing of wool with an acid dyesuff. As mentioned above, when the temperature of the dyebath reaches 140 deg. F., the RSO_3 ions are adsorbed at the surface of the fiber. When the layer of adsorbed ions has reached a certain thickness or concentration, depending upon the conditions of the experiment, adsorption tends to cease, since it is essentially a reversible action. Moreover, although the adsorbed substance forms temporarily part of the adsorbent, it is not chemically combined with it, that is, the fiber is not dyed. But the basic groups of the protein adsorbent combine with the adsorbed dye acid, forming an insoluble compound, and thus removes it from the system. The surface of the wool is now able to adsorb again, and adsorption followed by fixation proceeds until the material is dyed and the dyebath exhausted.

Weighting of Silk

The weighting of silk depends in the same way upon alternate adsorption and fixation of tannic acid or tin. When silk is soaked in a solution of tannic acid it adsorbs a considerable but definite quantity of the acid. Some of this may be combined chemically with the fibroin, but most of it is merely adsorbed, and can be washed away with water. When the silk is treated with a solution of an iron salt, the tannic acid is changed into an insoluble tannate, and the silk recovers its power of taking up tannic acid. Thus weighting is due to alternate adsorption and chemical action.

Chemical action in the liquid may also influence the result. The adsorption of soap by wool may be referred to in this connection. An aqueous solution of soap has an alkaline reaction, owing to the liberation of sodium or potassium hydroxide by hydrolysis, in accordance with the equation:

$$C_{17}H_{33}COONa + H_2O = C_{17}H_{33}COOH + NaOH$$

When wool is scoured with soap and water three bodies are present which can be adsorbed, namely, undecomposed soap molecules, fatty acid and alkali. The first of these is adsorbed until an equilibrium is attained, which depends upon the nature of the soap, the concentration of the solution, and its temperature. Scoured or washed goods practically always contain adsorbed soap. The free fatty acids are adsorbed also to a certain extent, but the alkali is taken up preferentially, so that the solution may become charged gradually with an excess of fatty acid which may either be present as such or form sparingly soluble acid soaps such as $C_{17}H_{33}COONa.C_{17}H_{33}COOH$. The alkali is at first taken up rapidly, but the rate lessens gradually until both alkali and fatty acid disappear at the same rate. Gradual elevation of temperature diminishes the effect of the secondary actions, adsorption of soap becoming gradually the chief factor.

Finally, the effect of an adsorbed substance on a chemical action may be referred to. When wool is stoved, only a comparatively small quantity of sulphur dioxide is required to bring about the chemical changes incidental to bleaching, but unless a large amount of adsorbed sulphur dioxide is present the bleaching is incomplete. The presence of an inert diluent in the chamber retards bleaching, whilst, when the concentration of the gas is high, better results are obtained. Evidently, the adsorbed sulphur dioxide must exercise some beneficial effect on the chemical changes which take place. The chlorination of wool is somewhat similar. Only a very small proportion of chlorine enters into chemical combination with the protein, by far the greater part of it being merely adsorbed, yet in the absence of this adsorbed chlorine unshrinkability is not produced.

—Dyer & Calico Printer.

General Dyestuff Release

The General Dyestuff Corporation as the sole selling agent of the General Aniline Works offers as a new brand of their own domestic manufacture, Fast Light Yellow E 2 G A, which from a Glauber's salt-sulphuric acid bath is said to produce on wool, bright greenish yellows of excellent fastness to light.

It is claimed to be extremely level dyeing and very suitable for combination shades. The fastness to steaming and hot pressing is stated as being very good, making it a very useful color for the dyeing of woolen piece goods for ladies' dress fabrics. Cotton, rayon or acetate silk effects are left perfectly clean.

In fastness to water, washing and perspiration it meets the ordinary requirements for this type of dye. It is also recommended for the dyeing of woolen yarn, especially carpet yarn and for combination shades on woolen and fur hats.

The American Laundry Machinery Company recently announced the acquisition of the General Laundry Machinery Corporation with the exception of the centrifugal section, formerly the Tolhurst Machine Works. The American Laundry Machinery Company is now one of the leading and by far the largest manufacturer of laundry machinery in the world. They expect to continue the manufacture of certain products of the general line at the factory at Chicago, and it is understood that they plan to employ a number of the sales representatives of the absorbed company.

Elementary Textile Microscopy

Part IV—Low Power Microscopy

Definition—Equipment—Mounting—Classifications—Yarns—Felts—Knit Fabrics—Braids and Laces—Woven Fabrics

By **JOHN H. SKINKLE**

Department of Chemistry, Lowell Textile Institute

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(Continued from issue of July 21, 1930.)

TO A bacteriologist, any work not using an immersion objective is considered as low-power work, but to a textile microscopist, low-power work means the examination of yarns or fabrics where individual fibers need not be observed.

Much of the work in textile microscopy may be done by the naked eye but is better done by means of a small magnification (cloth construction, slub examination and similar work), while other work requires magnification. In this discussion, therefore, low-power work is considered to mean the examination of yarns and fabrics at from zero to fifty diameters magnification.

Equipment

For very low powers (up to 10 x) pick glasses, pocket magnifiers, and similar simple microscopes may be used. For somewhat higher magnifications (5 x to 50 x) binocular microscopes may be used and are desirable for ease to the eyes and stereoscopic vision, but the ordinary microscope may be used with low power objectives such as the 48 mm. (2 x) and the 32 mm. (4 x) objectives. It is an interesting and useful fact to know that the 16 mm. objective with the front lens removed is approximately a 32 mm. objective and may be used as such to avoid the purchase of extra objectives.

Mounting

Large samples of yarn or cloth may be placed directly on the stage; if smaller samples are to be examined or if permanent samples are to be filed, the cloth or yarn may be placed between two slides and bound with gummed stickers. Where a bulge in the cloth prevents the use of two slides, the sample may be mounted on one slide by means of gummed labels.

In the case of open fabrics, a contrasting background may be desired and is obtained by placing white or black paper or cardboard behind the sample before mounting.

Cross-sections of cloth, especially rugs, being fairly thick, are best mounted permanently in a built-up cell on a glass slide.

Classifications

The realm of textile low power work may be classified as follows:

1. Fibers twisted into a continuous strand—yarns.
2. Fibers matted into a uniform fabric—felts.
3. One yarn looped about itself or several yarns about each other—knit fabrics.
4. Yarns twisted about each other progressively—braids.
5. Yarns twisted about each other in a complicated manner—lace.
6. Many yarns crossing each other at right angles—woven fabrics.
7. Uniform sheet with perforations—artificial lace.

A whole book could be written on any one of these divisions, but it will be sufficient here to indicate in general the desirable and undesirable features of each and allow the individual to study such special cases and sub-divisions as are necessary for more exact work.

Yarns

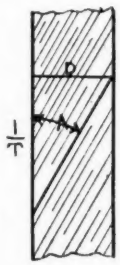
The information desired regarding yarns is generally the following:

1. The number and arrangement of the individual strands.
2. The size of the yarn.
3. The twist of the yarn.
4. The color and how it is obtained.
5. Any special finish.
6. The fiber or fibers used in the yarn.

Information as to the first division above is, in the cases of rayon and silk, limited to the number of filaments. Filaments may be counted in one mount but are more easily counted in several mounts. The best method is to make a cross-section and count the filaments from that. In the case of other yarns, such as cotton, the number of single yarns in a ply is easily determined as is the number of ply yarns in a cord. A cotton cord, for instance, might have two single yarns to a ply and six ply yarns to a cord—making twelve single yarns in all.

The size of the yarn is best obtained, in our present state of knowledge, by comparison of the diameter of the yarn with the diameters of the yarns of known count or denier and of approximately equal twist. Since the count of a yarn is expressed as weight per unit length or length per unit weight, the count is obviously a function of the square of the diameter but is also affected by the amount of twist—a larger amount of twist packing the fibers closer together and giving a smaller diameter to the same weight of fiber.

The twist per inch of a single yarn may be approximated from measurements as shown in the accompanying diagram where A is the angle of the fibers, T the number of twists per inch and D the diameter of the yarn in inches.



$$\tan A = \frac{D}{\text{inches per twist}} = DT$$

$$T = \frac{\tan A}{D}$$

Fig. 67. Angle of twist of a single yarn.

The measurement of the diameter is made by means of a micrometer and the measurement of A is made by means of a cross-hair ocular and revolving stage or by drawing the angle with a camera lucida followed by measurement with a protractor. The direction of twist is stated as right or left handed, the angle of the fibers in a right hand twist being upward to the right. Novelty yarns are sometimes spun with a corkscrew twist or with slubs.

If a single yarn is of a uniform color, the individual fibers should be examined. If the fibers are all alike, the color was obtained by dyeing the yarn or raw stock. If several colors of fibers are observed, the color was obtained by carding together two lots of raw stock of different colors—a grey color is often obtained this way. If fibers are seen which have two colors on the same fiber, the color was obtained by printing the roving in stripes and then re-carding and spinning. Ply yarns composed of single yarns of different colors may have been obtained by dyeing the single yarns before twisting; or if the yarns are of different materials, by cross-dyeing.

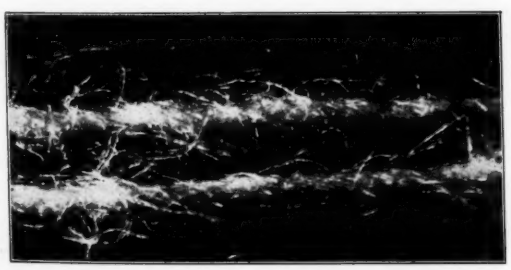


Fig. 68. Slubby yarn (20x)

If yarns are of uniform color but mixed materials, there is a possibility of union dyeing.

Special finishing processes sometimes given to yarns are sizing, detected by the presence of starch; singeing or gassing, detected by the absence of "hairiness" or projecting fibers; mercerizing, detected by examination of the fibers; waxing or oiling, detected by extraction with a solvent or by the Sudan dye test (See Section 38).

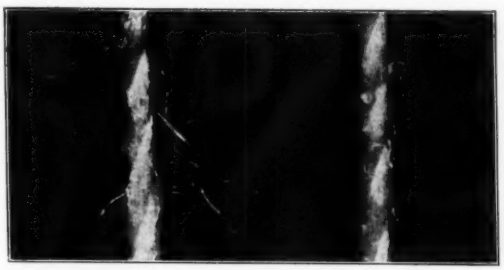


Fig. 69. Yarn before and after mercerizing (20x)

Felts

Felts are generally examined as to material, uniformity, and binding material.

Unless cotton batting be considered a felt, we may expect a sample to be composed wholly or in part of animal fibers, usually wool. Since felt consists of a tangled mass of fibers, only a qualitative estimate of the uniformity may be made. Binding materials are seldom used in felts except in the case of stiff felts used for some kinds of hats which may contain glue or some lacquer, these must be tested for chemically.

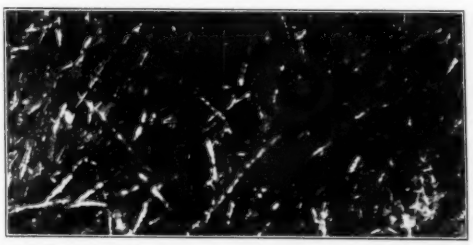


Fig. 70. Felt (20x)

Knit Fabrics

There are two general types of knitted fabrics—warp and filling knit. Warp knitting comprises only a small proportion of the total knitted output and is used principally in the manufacture of glove silk for underwear; filling knitting is used for most knitting and includes all hosiery. Warp and filling knitting may be identified by the fact that the former ravels lengthwise and the latter ravels crosswise of the fabric.

Warp knitting includes two stitches—the plain stitch, of which the three principal types are the Tricot, Milanese, and Atlas; and the rib stitch. Filling knitting includes three general types of stitch, although modifications of these stitches may be made: plain stitch, rib stitch and purl stitch. A satisfactory identification of these types

of stitches should be obtained by inspection of authentic samples.

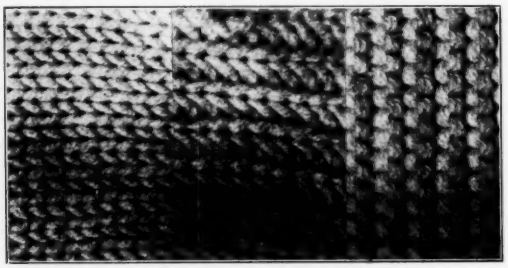


Fig. 71. Plain, rib, purl stitches (1¼x)

Methods of obtaining patterns in knitted goods may be obtained by one or more of the following methods:

1. By alternate feeding of colors—this gives horizontal stripes.
2. By plating, which gives one color on the face and another on the back.
3. By reverse plating, in which some yarns are reversed—this gives vertical stripes.
4. Tuck stitch, in which one thread is not looped but floats inside the back—this usually gives a diagonal pattern.
5. Draw stitch, in which one thread misses on the inside and floats on the back surface.
6. Drop stitch, obtained by leaving one or more needles out—this gives a ladder effect.
7. By twisting two differently colored yarns together and knitting—this gives no regular pattern and is called random knitting.
8. By adding a raised pattern or clock by means of a sewing machine.

Some modifications of knitted goods obtained by means of additional operations are:

1. Napping material.
2. Random dyeing, which would be identified by a random arrangement of colors, the same yarn would then have two different colors at different points.
3. Printed pattern—in which there would be a definite design and which could be identified by the fact that at the edge of the design one yarn would have two different colors.

Examination of knitted goods by a microscopist is usually confined to an examination of the yarn in the goods. Some of the more ordinary faults, exclusive of knitting errors, are the following:

1. Uneven yarns, causing streaks.
2. Streaks due to impurities on the yarns which prevent even dyeing, these impurities are generally gummed knitting oils.
3. Rust spots, usually with oil also present where lubricating oil containing a small amount of iron gets on the yarn.
4. Unevenly dyed areas in rayon goods where two different lots of rayon have been used.

Fig. 72. Uneven yarns in knit goods (20x)

Unless the microscopist has made a special study of knitting and knitted goods, examination of the goods for construction and pattern should be left to an experienced knitter.

Braids and Laces

These two types of fabrics are both made by twisting yarns, and the examination of them usually consists of an examination of the constituent yarns. The remarks made as to yarns in knitted fabrics also apply to these fabrics.

Woven Fabrics

Examination of woven fabrics includes the following determinations:

1. Pattern.
   a. Structural pattern.
   b. Color pattern.
2. Weaving or cloth defects.
3. Spinning or yarn defects.
4. Finish.

Examination of cloth for pattern will not be gone into here since the subjects of Cloth Design and Cloth Analysis are covered by many other books.

The more common weaving or cloth defects are the following:

1. Bad selvedges.
2. Broken warp threads—causing a lengthwise streak.
3. Broken filling threads—causing a crosswise streak.

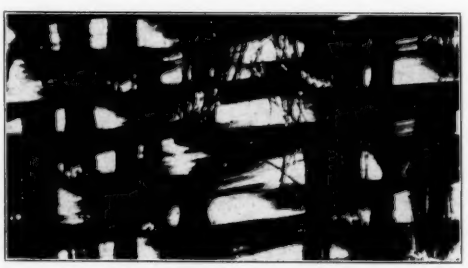


Fig. 73. Rayon cloth—broken yarn (20x)

4. Reed marks—causing a grouping of warp threads in two's, three's or four's.
5. Stains—due to oil, rust, dirt, or mildew.
6. Floats—in which a loose broken yarn floats on the surface.
7. In the case of rayon goods, "shiners" due to excessive tension on the rayon.

Fig. 74. Rayon cloth-knot (20x)

The common yarn or spinning defects are:

Fig. 75. Uneven yarns in cloth (20x)

1. Thick and thin yarns or "slubby" yarns.
2. Naps and motes or tangled fibers and pieces of leaf, stem or seed.
3. In cotton yarn—dead or unripe fibers.
4. Impurities such as oil or rust.

The various types of finish on goods are too many to be taken up in detail, but the following may be mentioned:

1. Grey goods—goods which have been neither bleached nor dyed.
2. Bleached goods — these are examined for oxycellulose.
3. Dyed goods—sometimes examined for evenness and penetration (by cross-section).
4. Printed goods.

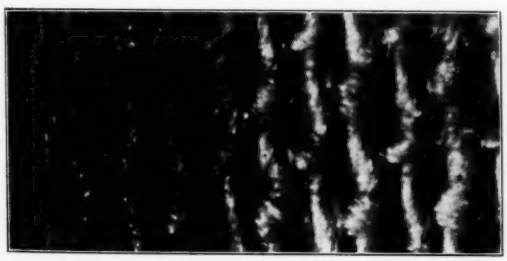


Fig. 76. Printed cloth (20x)

5. Shearing—recognized by numerous cut fibers on the surface.
6. Napped goods—recognized by the fuzzy surface.
7. Milled or fulled goods—recognized by a partial felting of the surface.
8. Cut pile goods—recognized by the cross-sections of fibers on the surface of the fabric and by U-shaped loops of fibers in the cross-section of the fabric.

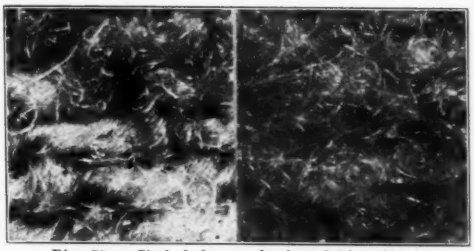
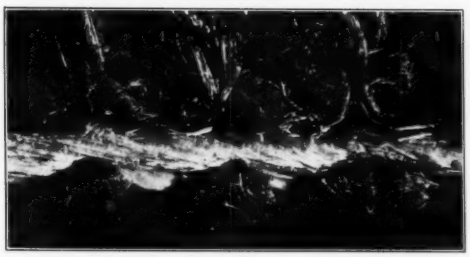


Fig. 77. Cloth before and after fulling (10x)



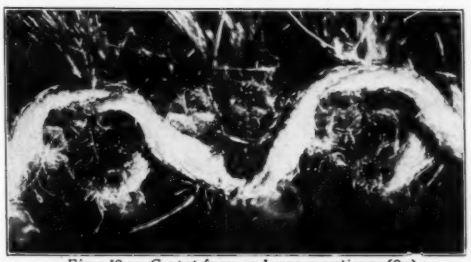


Fig. 78. Carpet-face and cross-sections (8x)

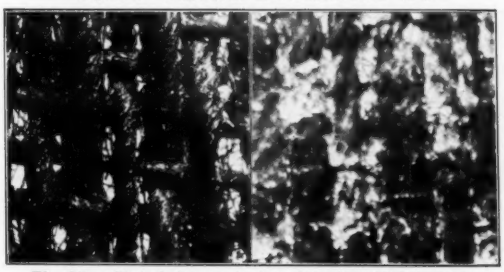


Fig. 79. Cloth before and after Schreiner Finish (20x)

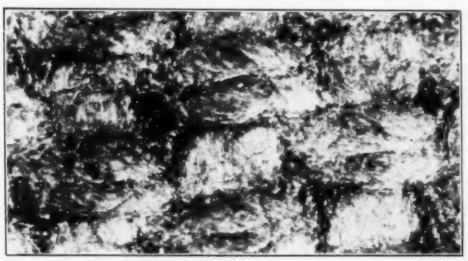


Fig. 80. Bookbinder's cloth—heavily sized and calendered (20x)

As in all other textile examinations, a good stock of authentic samples is of great importance to the microscopist in the examination of goods for finish and construction. Ordinarily, however, goods come to the microscopist, not for classification, but for the determination of the cause of defects; for this reason less attention has been paid to the types of fabrics than to microscopical and microchemical tests of fibers, yarns and fabrics.

(*To be continued.*)

The Chlorination of Wool for Unshrinkable Finish

By **ALBERT PARSONS SACHS**

WOOL has the properties of warmth and comfort to a degree possessed by no other textile fiber. Cotton has certain physical properties of a highly desirable character which make it particularly suitable for use where the garments produced are to be subjected to ordinary domestic washing. Under the conditions of washing with warm soap solutions, woolen garments tend to mat or felt and to shrink, particularly if they have been in contact with perspiration for considerable periods or have been subjected to abnormal amounts of friction.

It is by no means impossible to wash woolen garments with dilute cold suds, avoiding excessive handling and shaping the garments during drying so as to avoid any considerable degrees of felting and shrinking, but hosiery and knitted goods in general, underwear, blankets, certain varieties of flannel garments, and uniforms used in hospitals or other public institutions generally require vigorous washing. For such articles, washing properties similar to those of cotton would be highly desirable. Such properties it has been attempted to attain by subjecting wool to chlorination to produce what is known as the "unshrinkable" finish.

Chlorination of Wool Leads to Change in its Properties

The chlorination of wool leads to a definite change in the properties of wool. Normal wool fiber consists of three well-defined zones. There is an outer covering or epidermis of overlapping scales attached to a mass of fibrous substance or cortex which constitutes the major bulk of the fiber and gives it most of its strength; within the cortex is a cellular canal containing most of the natural coloring matter of the fiber.

In an interesting article in Melliands Textilberichte[1] Prof. Alois Herzog describes the visible changes in wool occurring on treatment with acidified bleaching powder (free chlorine). His excellent photomicrographs show the changes which occur in chlorinated wool. The chlorinated wool tested by him, which was probably over-chlorinated, not only has an increased affinity for dyes (particularly basic dyes) but shows differences as compared to normal wood in behavior toward practically all the stains and reagents used in microscopic work. Staining with methylene blue or safranin enables differences in the cross-sectional character of the two wools to be clearly visible. However, it is probable that Professor Herzog was working with wool which was, from the commercial point of view, over-chlorinated. In what is probably the most authentic article on chlorination of wool yet published,[2] S. R. Trotman says that in properly chlorinated wool the outline of the epithelial scales remains perfectly plain and the affinity for dyestuffs is not increased. An increase in the affinity for dyestuffs is considered by Trotman as an indication of over-chlorination with attendant loss in wearing qualities of the wool.

J. R. Adams[3] finds no difference in the uptake by chlorinated and unchlorinated wool of the characteristic acid dyes Orange II and Lake Scarlet R. Dyed chlorinated wool sometimes shows a greater brightness, but this is due to the increased glossiness resulting from the chlorination and possibly to the residual acid present in the chlorinated wool. Adams'

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[1] 1928, pp. 33-38
[2] *Jour. Soc. Chem. Ind.*, 1922, *p.* 219*T*.
[3] *Jour. Phys. Chem., vol.* 27, 1923, *pp* 81-84.

experiments confirm Trotman's result and show that an increased affinity for dyestuffs is characteristic only of over-chlorinated wool. This increased affinity for dyestuffs is not uniform and leads to non-level dyeings.

Felting Properties of Wool Due to Interlocking of Epithelial Scales

It is fairly well understood that the felting properties of wool are due to the interlocking of the epithelial scales. Wool fibers without scales will not felt. The function of chlorination is to attack these scales and thus render wool non-felting and non-shrinking. It has been possible to scrape the scales from wool fibers by a set of accurately adjusted knives. Such scraped wool shows only the slightest tendency to felt and shrink even after prolonged working in warm soapsuds. This method of mechanical scraping is not at all commercial. S. R. Trotman believes the felting to be due to the epithelial scales, while shrinkage is a property of the cortex. Examination of hundreds of samples of chlorinated wool indicated there is no relation between shrinkage and destruction of epithelial cells, but the felting power decreased with increasing damage to the epithelial cells. Speakman's results, mentioned a little later, indicate the probable cause of elimination of shrinkage by chlorination of wool.

Action of Chlorine on Textile Fibers is a Various One

So much for the present for the structure of wool. The action of chlorine on textile fibers is a various one. For cotton, chlorine is the admirable bleaching agent universally used. Chlorine does not bleach wool, but tends rather to yellow it, and directly attacks the fiber. In the case of mild treatments with chlorine, the scales are first attacked, as they constitute the epithelial or surface layer. In this case yellowing does not occur. The microscope shows that first the edges of the scales are rounded and the scales are either loosened or converted into a viscous, gelatinous material. Upon heavy chlorination the entire fiber is converted into a yellow, viscous mass. Chlorine reacts with nitrogen and sulfur of the wool (keratin) molecule so that chlorinated wool shows lower percentages of these elements than the original unchlorinated wool. Trotman claims that properly chlorinated wool contains practically no chlorine, soluble or combined. For example, a properly chlorinated wool contained only a trace of soluble chlorine and 0.007 per cent of combined chlorine, while an over-chlorinated wool contained 0.033 per cent of soluble chlorine and 0.079 per cent of combined chlorine. Natural wool contains only traces of combined chlorine.

M. Ernotte states[4] that the scales resist chlorination better than the cortex and that it is the outer surface of the cortex which first chlorinates to a gelatinous mass from which the scales very easily detach in subsequent washing or scouring. Ernotte also proposes to increase the strength of the chlorinated fiber by hardening the gelatinous capsule in which it is encased; he claims to have had excellent results by after-treating with bichromate solution.

In a paper read before the Yorkshire Section of the Society of Chemical Industry[5] on "The Chlorination of Wool" J. B. Speakman and A. C. Goodings point out that chlorination to the extent involved in good commercial practice causes no apparent drastic action on the fiber, but subsequent treatment with soap or soda solutions causes the outer layers of the wool fiber to gelatinize and swell enormously. A zone of jelly is thus created between the epithelial scales and the unattacked core of the fiber. This jelly layer is the true cause of the unshrinkability because it renders the scales incapable of causing the fiber-travel which is the immediate physical cause of shrinkage. But this jelly layer and its sheath of scales are easily removable by vigorous washing and by friction and result in poor wearing properties. It would appear possible to restore good wearing properties if one could cause the gelatinized layer to shrink and harden centrally toward the unattacked core of the fiber. But to insure true unshrinkability sufficient chlorine must be used to cause the scales to gelatinize partly as well as part of the cortex, thus making it difficult to achieve exactly the correct conditions. Experiments made with chromium mordanting of chlorinated wool did in fact impart good wearing qualities to the chlorinated wool, a fact confirmed by M. Ernotte. This means that properly chlorinated wool yarn should be dyed with chrome dyes. Other agents might be found for undyed yarns.

Wool also Undergoes a Change in its use Properties

Alongside of the changes thus observed, the wool undergoes a change in its use properties. The milling properties are lost, the mass of fibers no longer felts and fabrics or garments become practically unshrinkable. In addition there is an increased tendency to take up dyestuffs, if the chlorination has been carried too far. Also the surface is glossier.

The exact course of the chemical reactions occurring is obscure. Chlorine is taken up by the keratin to form what we may call chlorokeratin. This contains insoluble chloramine groups. Further action of chlorine leads to the formation of more soluble types of compounds leading finally to the yellowing, sometimes unfortunately occurring in the process. This yellowing is always a sign of over-chlorination. As might be expected, the effects of chlorine are intensified by the use of high concentrations and high temperatures.

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[4] *L'Industrie Textile for* 1928, *pp.* 155-6.
[5] *Nov.* 15, 1926.

Commercial Chlorination Must Be Carried On With Great Care

Commercial chlorination must be carried out with great care and in moderate concentrations. When the edges of the scales show erosion, the treatment must be stopped, as beyond this further treatment attacks the horny surface to which the scales are attached and exposes the cortex. The cortex consists of bundles of extremely minute fibers or fibrillae which, when thus exposed, easily split and sever and yield a material with low resistance to rubbing and friction and low wear value. Consequently cold dilute solutions of chlorine are best, and hypochlorous acid is much better than chlorine itself.

In the article previously quoted, Trotman shows that free chlorine causes damage whereas hypochlorous acid does not. Chlorine in water exists in equilibrium with hypochlorous acid and hydrochloric acid as is shown by the following equation:

$$Cl_2 + H_2O = HOCl + HCl$$

Under certain conditions the chlorine exists chiefly as chlorine and under other conditions chiefly as hypochlorous acid. If bleaching powder is treated with hydrochloric acid, the available chlorine exists chiefly as actual chlorine, but if the bleaching powder is treated with boric acid the available chlorine exists practically entirely as hypochlorous acid. Hypochlorous acid is far less injurious to the wool fiber than chlorine. Trotman found that the use of not more than 2 grams of available chlorine per liter liberated as hypochlorous acid by boric acid practically prevented any damage to wool, whereas if mineral acid were used not more than 0.6 grams of available chlorine per liter could be safely used. An excess of either hypochlorous acid or chlorine causes destruction of both epithelial scales and cortical cells, considerable losses in weight, high solubility and bad wearing qualities. However, most of the properties usually ascribed to chlorinated wool are characteristic only of over-chlorinated wool.

Different wools react differently and over-chlorination is an ever-present threat. In cases of over-chlorination the appearance is affected by the formation of brownish patches impossible to remove. Unshrinkability is thus indeed obtained, but at the cost of strength. Under-chlorination preserves the strength but does not provide unshrinkability.

In The Wool Record and Textile World[6] J. & J. C. Schofield give the average concentrations as 1.6 oz. to 5.3 oz. available chlorine per liter, but these are undoubtedly far too high as may be seen from Trotman's figures.

A Treatment Recommended

A treatment recommended is to wet out goods for ten minutes and slowly to add 5 per cent on weight of goods of chlorozone, and allow the goods to work for ten minutes to insure uniform saturation. Then 10 per cent of 40° Bé. muriatic acid is added, the goods worked for one half hour, the bath discharged, the goods rinsed with dilute bisulfite and finally rinsed completely. The fabric is described as practically unshrinkable and of a somewhat harsher, less "woolly" handle than ordinary wool, although the difference is discernible only to an expert hand. In L'Industrie Textile[7] the writer claims the treatment can be applied to practically all dyed fabrics, as most dyes are unaffected. The details of producing the chlorine and the types of vessels required, the precautions for ventilation which must be taken, represent engineering considerations of great importance, but they need not be given here.

Yarns are treated in hanks in well-cleaned "becks" or modified Hussong machines. Piece goods and hosiery fabrics are best treated in open width and not in rope form. The bath must remain on the acid side at all times and the rinsing must be thorough. It is advisable to "kill" excess chlorine after the chlorination with a dilute bisulfite bath; piece goods may receive a mild sulfurous acid bleach in the dolly scouring machine. The amount of chlorine necessary is 2-2½ per cent on the weight of the wool, but it should be added gradually to the chlorinating bath.

The Best Wools Do Not Withstand Chlorine Best

The best wools do not withstand chlorine best. Fine Botany types are most seriously affected by chlorine, while mountain-grown wools resist best. In spinning wool fibers for a flannel to be chlorinated, the yarns must be spun tighter to add strength to final fabric. In weaving, the setting may be closer than for ordinary standards. It is unnecessary to nap the goods, as ordinary wear will tend to raise a nap. After scouring and milling to correct weight per yard, the goods are chlorinated, rinsed, London shrunk and cold pressed to yield a flannel of very stable characteristics. A second London shrinking will not reduce a 60-yard piece more than a half yard in length nor a 56-inch width more than a half inch. Garments 60 inches long made from this flannel and regularly worn and subjected to fortnightly laundering and sterilization, after a year's use showed a shrinkage of not more than 3 per cent, which means the garments were unshrinkable.

It has been attempted to use formaldehyde on wool (similarly to its action on gelatin) to produce unshrinkability, but the cost is too high compared to that for chlorine.

A Criterion for Over-Chlorination

Trotman establishes a criterion for over-chlorination. Microscopic examination should show but more than 5 per cent of damaged fibers. Commercial chlorination may result in 5 to 50 per cent of damaged fibers. It may be taken as an absolute rule that bad wearing qualities of "unshrinkable" wool are asso-

[6] *October* 25, 1928.
[7] 1927, *p.* 332.

ciated with over-chlorination as determined by high percentages of damaged fibers.

With respect to the other properties of chlorinated wool, the following figures taken from Trotman's work may be of interest. The tensile strength and elasticity of properly chlorinated wool, contrary to general opinion, are not adversely affected.

Elasticity of original untreated wool yarn..... 1.50
Elasticity of undamaged chlorinated yarn..... 1.60
Elasticity of slightly damaged chlorinated yarn.... 1.52
Elasticity of damaged chlorinated yarn..... 1.375
Elasticity of badly damaged chlorinated yarn..... 1.295

Using the same yarn which was, however, chlorinated by a different method, the following results were obtained:

Elasticity of untreated wool yarn..... 1.50
Elasticity of undamaged chlorinated yarn..... 1.62
Elasticity of damaged chlorinated yarn..... 1.475

The results for properly chlorinated material are not surprising, because the strength of the wool fiber resides in the cortex and not in the scales and it is only the scales which are attacked under conditions of proper chlorination.

It has already been pointed out that an increased affinity for dyes is a sign of over-chlorination and is an index of bad wearing qualities to be expected. The increased depth of dyeing is proportional to the percentage of damaged fibers.

The wetting power of properly chlorinated wool is just a little greater than that of ordinary scoured wool but increases with increased percentage of damaged fiber. In addition the easily wet samples are particularly weak when wet and in cases of extreme over-chlorination the wet fiber becomes soft and almost slimy. Most of the original strength is regained on drying. This behavior is similar to that of some of the artificial fibers (*i.e.*, artificial silks). It is not shown by properly chlorinated wool. This phenomenon is particularly noticeable after soaking in dilute caustic or soda solutions.

Properly Chlorinated Wool Loses Little Tensile Strength

A sample of properly chlorinated wool which had a tensile strength of 2.59 when dry had this decreased only to 2.58 by soaking in decinormal soda solution, while an over-chlorinated sample with a tensile strength of 2.52 when dry had this decreased to 1.80 by a similar soaking in the same soda solution.

The regain for properly chlorinated wool is about the same as for untreated wool, but the regain increases with increasing percentages of damaged fibers.

The solubility of properly chlorinated wool in water, dilute caustic solution, dilute soda solution or dilute acetic acid and salt solution (artificial perspiration) is no greater than that of ordinary wool, but the solubility in each of these media increases with increasing percentages of damaged fibers in the chlorinated wool. A sample of properly chlorinated wool treated with decinormal caustic soda solution for three hours lost 6.29 per cent, while an over-chlorinated sample lost 16.52 per cent. A twelve-hour treatment with "artificial perspiration" caused the properly chlorinated wool to lose 0.90 per cent while the over-chlorinated material lost 4.05 per cent.

Summary

1. Chlorination of wool causes the loss of felting and shrinking properties.
2. Chlorination of wool must be strictly controlled to ensure uniform action and must be stopped when not more than 5 per cent of the fibers show damage upon microscopic examination.
3. Chlorination is best carried out by the use of hypochlorous acid (easily prepared by the action of boric acid on bleaching powder).
4. Properties other than felting and shrinking are not appreciably affected by proper chlorination as defined above.
5. Over-chlorination causes yellowing of fiber, loss of tensile strength and elasticity, increased wetting power, increased regain, increased affinity for dyestuffs, lowered resistance to water, perspiration, caustic and soda and loss in wearing properties.

[Editor's Note—*Dr. Richard Feibelmann states that Aktivin attacks wool fiber less destructively than a hypochlorite, and that wool treated with Aktivin dyes deeper shades even than wool that has been chlorinated by a hypochlorite. Furthermore, he states that Aktivin chlorinated wool is less damaged physically. Another common use of the chlorination process in connection with wool is a preliminary treatment for wool materials that are to be printed, and Aktivin has been successfully used for this purpose. No information is at hand however comparing the hypochlorite with the Aktivin treatment as far as unshrinkable finish is concerned.—L. A. O.*]

—*Bulletin of the Nat'l Ass'n of Wool Manufacturers.*

Ponsol Violet A R Paste

The Dyestuffs Department of E. I. du Pont de Nemours & Co. has placed on the market an addition to their line of cold dyeing vat colors, to be known as Ponsol Violet A R Paste. This is a violet of brilliant reddish shade and is recommended not only for all types of cotton dyeing but for use on silk and rayon materials as well.

Ponsol Violet A R Paste is said to be extremely fast to light and may be used alone or in combination where a violet of the best possible fastness to light, washing, fulling and stoving is desired. It is stated that this product is suitable for application on the circulating types of closed machines as well as the jig and padder as it exhibits good penetration, is level dyeing and is practically unaffected by copper or monel metal.

This violet is not recommended for printing, but as it discharges to a clear white with sulfoxite CL, it may be used as a ground for color discharges when a vat violet is desired.

Between Two Worlds

A Journey Through the Domain of Colloid Chemistry

By **JUSTIN HAUSNER**

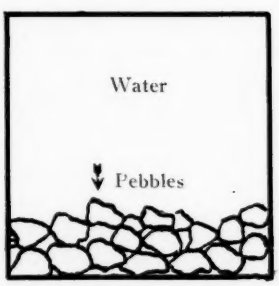
Specially Translated for the American Dyestuff Reporter

CATCH-WORDS have a decided influence upon most people; they give impulse and purpose to community projects. This is true, not only of our community life, but of scientific life as well. As soon as a new field, or new ideas, open up before the pioneers who are struggling in noble emulation in the forefront of the advancement of knowledge, the interest of the whole band of investigators is directed to the newly-discovered problems, and we speak with enthusiasm, in catchwords, of the prospect newly unrolled before us. Such a modern catch-word (perhaps nowadays we should call it a "slogan") is the familiar "colloid." What reader has not met with this word, in speech and in writing? A number of years ago, at the beginning of the "War of Colloid Chemists," as a certain period of controversial discussion has playfully been called, Wolfgang Ostwald, the son of the famous creator of the theory of color, gave to his excellent introduction to modern colloid chemistry the title "The World of Neglected Dimensions"; yet this designation has as good as lost its justification, for colloid chemistry has, since that time, met with ever-increasing attention, has forced its way into ever-broadening fields, and has exerted a strong influence upon the present state of our chemical knowledge. We textile specialists, nowadays, are simply assuming, in every case, that, in our field of work, practically everything is probably a matter of colloidal behavior. It may, then, be not without interest for us to take a general view of our world from the standpoint of the colloid chemist. This is the purpose of what follows.

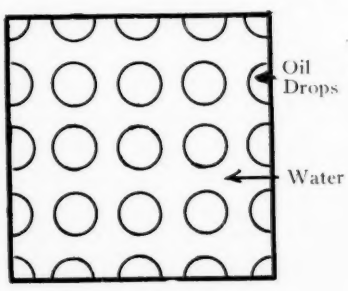
Although, about sixty years ago, the English chemist Thomas Graham carried out researches upon the diffusion of typical colloids, still, the concept of colloid (derived from the Greek word "kolla" = glue) has in the meantime continuously altered, and colloid chemistry, which rests upon the basis of views held to-day, is a young science. For the understanding and explanation of colloidal phenomena, it is necessary to become familiar with certain fundamental concepts.

Now, if we consider a portion of space limited on all sides, a space which is filled with any one substance (or several), science calls this a "system." If this system displays in all its parts the same properties, it is called a homogeneous system; if in different parts it displays unlike properties, we have to do with what is called a heterogeneous system. A flask filled with water, therefore, would form a homogeneous system; but, if we were to drop into the water a few pebbles, for example, then the contents would form a heterogeneous system, for the mixture possesses, in the space taken up by the water, other properties than does that space which is filled by the pebbles. In colloid chemistry, we are interested only in heterogeneous systems, that is, those which are formed of several different components. Heterogeneous systems, whose properties periodically alter in all directions, we call disperse systems. Disperse systems, therefore, form only a special case of heterogeneous systems. The concept of a homogeneous and of a disperse system will be made more clear through the schematic illustration here given:

Homogeneous System
(properties are the same in all parts of the system.)



Heterogeneous System
(properties are different in the different parts of the system.)



Disperse System
(properties alter periodically in all directions.)

Though in the above the concept of a disperse system is clearly defined, yet I have not spoken definitely of the dimensions of the different particles of substance involved. Since, however, many properties of disperse systems are strongly influenced by this matter of dimensions of particles, it is important for us to become exactly acquainted with these relations.

A suspension of the most finely ground clay in water forms a uniformly turbid liquid. The separate particles of clay can no longer be distinguished by the eye alone, and only the microscope gives us any information regarding the presence and the form of the particles. Such a disperse system, which after long standing "settles" and separates into two layers, is called a coarse dispersion. To this group, for example, belong the pastes of insoluble dyestuffs, made up with water, or the precipitates frequently produced in the operations of analytical chemistry. Another criterion of coarse dispersions is, that they can be easily separated into their constituents by filtration through ordinary filter paper.

Now, if we put a few blue crystals of copper sulphate into a sufficient amount of water, we shall soon notice that the space which the crystals at first filled is gradually becoming smaller, that the water is becoming colored blue, and finally that no more solid copper sulphate is visible. We say that the copper sulphate has dissolved in the water. After uniform mixing of the liquid, we can no longer perceive the particles of copper sulphate, either with the naked eye, or—in contrast to the coarser state of dispersion—in the microscope, even with the strongest magnification. The molecules of copper sulphate have forced themselves in a very uniform way between the molecules of water. (We shall disregard in this connection the dissociation of the molecules into ions.) An experiment will show us further that filtration of the blue solution, as we well know, can accomplish no separation of the copper sulphate from the water. Disperse systems of this sort are called true or molecular solutions, or, simply, solutions. True solutions are, therefore, distinguished from coarser mixtures by the fact that in the latter the particles are visible under the microscope, at least, and that the system can be separated into its constituents by filtration through common filter-paper. These two properties are in immediate independence upon the size of particles which form the system.

Since nature, as we know by experience, never makes a leap ("Natura non facit saltum"), but always displays transitional stages between extremes, we might suspect that a transitional region exists between the world of coarse subdivision and that of molecular solutions. If we consider the particles of a coarsely subdivided system, that is, e.g., of a suspension of clay in water, as continuously becoming smaller, we should finally come to a limit where the particles would no longer be recognizable in their own form, even under the microscope, nor could they any longer be retained by filtration through filter-paper. A so-formed disperse system, which would then display externally a similarity to a true solution, would possess, however, certain properties which would distinguish it sharply from a true solution. An aqueous solution of Congo Red gives a perfect impression of a molecular solution, both to the naked eye and with the microscope, and it passes through filter-paper completely without leaving any residue. But if the solution is carefully covered with a layer of water, the water being so carefully poured on that the layers do not mix, and, as a parallel, we do the same with a solution of copper sulphate, we shall after a time perceive that the copper sulphate solution is of itself forcing its way slowly into the super-imposed layer of water, or, as we commonly express it, is diffusing into the water; while in the case of the Congo Red such diffusion takes place hardly at all. The difference between the two solutions is still more plainly evident through the following experiment: A glass cylinder, open at each end, has over its lower end a sheet of parchment paper or of some animal membrane (as a prepared sheet of a bladder, fastened on tightly). This vessel is supported in a vertical position in a larger vessel filled with water (fig. 1).

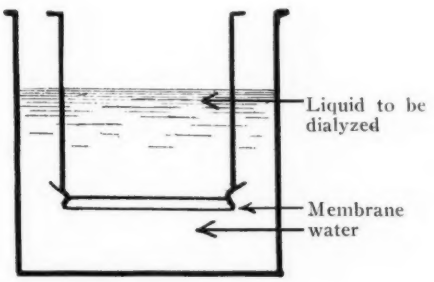


Fig. 1. Dialyzer.

In the inner vessel is placed, for the first experiment, a solution of copper sulphate, in the second case a solution of Congo Red, in each case the level of the liquids within and without being the same. After some time we shall observe that the copper sulphate solution, in contrast to the Congo Red solution, has passed through the membrane into the water, as can be easily recognized by the color of the water. As we express it, the copper sulphate solution is dialyzable, while the Congo Red is not. The apparatus we have used is called a dialyzer. If we look upon the membrane, which we have used, as a filter whose pores are of very small diameter, we can see that between the copper sulphate and the Congo Red solutions the same difference, in principle, exists as does between a coarse-suspension system and the Congo Red solution. The particles of the latter substance, then, are of larger size than are those in a true solution, and than the diameter of the pores of the diffusing or dialyzing membrane. Disperse systems whose particles are smaller than those of the coarse-suspension system, and larger than those of true solutions, are called by the general term of colloids. The domain of the colloids lies between the

region of coarse subdivision and that of true solutions; it is a world by itself, a world in which matter possesses special, peculiar properties. Colloids are distinguished from coarse subdivisions by the fact that they are not filterable, and that their particles are not visible under the microscope; they are distinguished from true solutions by the fact that they do not dialyze.

The boundaries of the colloidal domain, limiting it from its two neighbors, are not, however, very sharply defined. There are disperse systems, whose size of particle rests upon the boundary line, so that the properties of the one of the three areas are continuously passing over into those of the other state. As a typical colloid, however, we should designate, in general, such disperse systems, the size of whose particles lies between 1/10,000 and 1/1,000,000 mm. The following table will make this statement more clear:

	Filtration	**Dialysis**
	Separable through	Separable through
Coarse subdivisions	**Colloidal solutions**	**Molecular solutions**
Size of particles greater than 1/10,000 mm. Particles visible under the microscope.	Size of particles from 1/10,000 mm. to 1/1,000,000 mm. Particles no longer visible under the microscope, but detectible under the ultramicroscope.	Size of particles less than 1/1,000,000 mm. Particles no longer visible by optical means.

Colloids display certain other interesting properties, beside those already mentioned. If we study a colloid solution under the microscope, not, as commonly, in transmitted light, but under laterally-translated illumination, we are able to observe the flashing of the rays of light refracted by the dispersed particles, even though we cannot observe the shape of the separate particles. In true solutions, however, this phenomenon is not noticeable. Since it is this optical arrangement, then, which makes possible the detection of particles beyond the range of visibility of the ordinary microscope, we call such an arrangement the "ultra-microscope".

A similar phenomenon may be observed with the naked eye, when we pass a pencil of light through a colloidal solution. While, in pure water or a true solution, the path of the beam cannot be traced, it is plainly visible in the colloidal solution, through a cloudy illumination which arises in and along the path of the beam of light. This phenomenon possesses a great similarity to the familiar one of a sunbeam passing through dust, as is often noticed in a room; a phenomenon which is generally known as the Tyndall phenomenon.

When once the colloidal condition has been recognized as a disperse system, of a definite degree of particle-dimension, the question naturally arises, whether any substance whatever may not be transformed into the colloidal state. Now, while in earlier years we knew of only a few typical colloids, we have been able to form more and more of them as time has gone on, and we now possess methods by which we can transform practically any substance into the colloidal state. Two ways, in general, lead into the world of colloids, the one through the country of coarse subdivision, the other through the realm of true solutions.

If we wish to prepare a colloidal solution of silver, we can start with simply ordinary, massive silver, and disintegrate it, by Bredig's method, through the electric arc, which, for example, is passing between two silver wires which are dipping into the dispersive material, such as water. Soon we perceive a cloud of colloidal silver rolling away through the liquid from the silver wires. Then, too, very fine grinding of substances in the so-called colloid mills, which are charged with the dispersive agent, can be used to disintegrate substances to the colloidal magnitude of particle.

In the other way, leading through the realm of true solutions, the molecules contained in these are united to molecular complexes, until these have reached the size of particle of the colloid state. If, for example, we treat a solution of a silver salt under the proper conditions with a reducing agent, we often obtain splendidly colored green, blue, or red colloidal silver solutions. Not all substances are so inclined to the formation of colloidal solutions. Often the colloidal state is only an unstable intermediate stage on the passage from a true solution to a coarsely-subdivided state. Then, as we express it, the colloid flocculates, at the boundary of the colloidal zone. The flocculated substance we call a gel, and the colloidal solution, from which it flocculated, a sol. If we wish to hinder the flocculation of a sol, we can maintain the colloidal condition artificially by adding to the solution a so-called protective colloid. These protective colloids are substances which possess so great an inclination to form the colloidal state that their particles surround the particles of the colloid to be protected, and so keep the latter from separating out as a gel. The albumens, e.g., are protective colloids for colloidal solutions of the noble metals.

According to whether we are dealing with solid, liquid, or gaseous substances which form the system, we speak of

(a)—suspensions, if solid substances,
(b)—emulsions, if liquid substances,
(c)—foams, if gaseous substances,

An example of a suspension is the solution of Congo Red, to which reference has already been made. A typical emulsion is common milk. Colloidal foams have up to the present been studied to only a slight extent. The dispersive agent in a colloidal system does not need always to be a liquid. Ruby glass, for example, is colloidal gold dispersed in glass; fog is water colloidally dispersed in air.

An interesting group of colloids is composed of the gelatins, or rather jellies, which combine the properties of the solid and liquid states. Upon being warmed, jellies soften slowly, and so possess no sharp melting-point; and on cooling they pass back again, slowly, to the solid state. Their mode of formation, too, is interesting. They are formed either by cooling of liquids or by swelling of solids.

Colloid chemistry, as already mentioned, plays an especially important part in the textile operations of dyeing,

printing, and finishing. This is not surprising, when we recall that the textile fibers, as well as a large number of the substances employed by the textile technician, possess the colloidal character.

To-day, we consider almost all textile fibers as gels, which possess a pronounced capacity for swelling. With this property, the power of taking up dyestuffs goes hand in hand. Naegeli compares the structure of a fiber to a brick building. The separate bricks in this parallel, whose uniting medium, the mortar, consists of organic substances, he calls micelles. These micelles we to-day regard as the particles in a colloidal system.

In earlier years we used to puzzle our heads as to the processes which went on in the production of a dyeing upon a textile fiber. For years, a bitter controversy has been waged over the question as to whether dyeing is a physical or chemical process. To-day we consider that a single theory of dyeing is not capable of explaining all of the phenomena involved, but that, rather, both chemical and physical forces are at work in the process of dyeing. In some cases, however, only a consideration of the process from the colloido-chemical standpoint can afford in illuminating explanation. Thus, for example, the production of a dyeing upon cotton with a substantive dyestuff, otherwise so difficult to understand, is easily to be understood from the colloido-chemical standpoint. On swelling of the cotton fiber, the spaces between the micelles first increase. The colloidal particles of dyestuff then slip between into these expanded intermediate spaces, and are then held fast upon the inner micelle-walls through adsorption.

In the operations of printing, too, quite similar processes appear to be at work. In this case, a further colloidal medium, the printing-paste thickener, also comes into the circle of operations. Haller, who was the first to dispel the darkness which overhung these operations, ascribes to the thickener a colloidal structure with interspaces, which, as we can see, take up and hold the dyestuff, the mordant, and such other substances as are involved. On steaming, these substances gradually migrate upon the fiber, while the thickener, e.g., the starch, is dissolved by chemical breaking-down; or else this migration is made possible by the dilation of the interspaces of the thickening-agent, a process which is similar to that already described under the swelling of fibers.

A purely colloido-chemical chapter of textile technology is formed by the processes of finishing, since practically all finishing-materials, as the starches, gums, glue, etc., are colloidal substances, which in fact are so much so that they are the most suitable for use in the study of colloidal phenomena.

Starch, in particular, is a characteristic example of how much influence the degree of subdivision of a substance has upon its value in practical use. Starch swells in water at a certain temperature, which is characteristic for the various kinds of starch, and in so swelling passes into the form of the well-known starch-paste. This possesses all the typical properties of colloids; it gelatinizes upon cooling, cannot be dialyzed, and upon standing flocculates as a gel. If we try to filter starch-solutions through a paper-filter, we notice that, according to experimental conditions, a varying amount of unfilterable material remains upon the filter. Starch paste therefore contains some particles of a larger size than those of the colloidal grade.

But, if starch paste is boiled for a considerable time, or for a shorter time under pressure, it gradually becomes thinner and more transparent, and more similar to a true molecular solution: as we express it, the starch has become soluble—"opened up." This change in the starch paste takes place more easily if, on heating the starch paste, we add some "opening-up" agent, such as enzymatic substances—Diastafor, Degomma, Biolase, or some oxidizing agent, as Aktivin. These opened-up starch-pastes are also true colloids, and are distinguished from the original, thicker pastes, only through the higher degree of dispersion of their particles, which imparts to these pastes the appearance of a true molecular solution, and makes it possible for them to penetrate deeply into the interior of the knitted or woven goods. This penetrative power is what gives such pastes their great value in the process of finishing. When we try to filter such an opened-up paste through common filter-paper, we observe that only very little material remains upon the filter-paper, which is again the consequence of the small dimension of the particles in the disperse system. On cooling, these opened-up pastes gelatinize just as do the original, thick pastes, and they may also, after standing for awhile, flocculate. Attempts to dialyze these opened-up pastes makes it appear probable that they cannot be looked upon as true solutions, since they will not dialyze. This, however, does not quite hold true for pastes which have been opened up by enzymatic re-agents, since such pastes do contain more or less dialyzable material, according to the length of time and the temperature prevailing during the enzymatic action. But these dialyzable substances are no longer starches, but rather their degradation products, particularly sugars, which to some extent at least no longer give the iodone-starch reaction. By further breaking down of the starch molecule to smaller molecules, the degree of dispersion of the particles naturally decreases also, until we come gradually into the region of true, dialyzable solutions. The last degradation-product of starch, glucose, according to the sequence

Starch→soluble starch→dextrine→maltose→glucose,

possesses, in solution, perfect molecular properties.

Another important group of textile materials is formed by the soaps, Turkey-red oil, etc. The stability of the colloidal state which their solutions display is the chief reason for their technical use. These substances possess to a high degree the properties of protective colloids; they hold in suspension particles of fat, greasy dirt, lime soaps, etc., and so hinder them from separating out in undesirable places and ways.

In returning from this excursion of ours into the colloid kingdom, if we cast a glance backward by way of review,

the importance of the relatively youthful science of colloid-chemistry will be clearly comprehensible. It is in a position to co-ordinate many detached, separate phenomena from a single viewpoint, without exception, and in such a way as to extend their importance still further. It teaches us how much importance the size of particles of a system possesses, and what great help we can draw from it for our industries—help partly already appreciated, and partly still unforeseen.

The Commerce of Chemistry*

By J. N. TAYLOR
Chemical Division, Bureau of Foreign and Domestic Commerce

A GLANCE at the pages of history will show the close relationship which chemistry has held with the advance of the human race. From earliest times, as evidenced by Biblical records, as well as by the monumental records of Egypt, and the writings of Herodotus and Pliny, chemistry as an art played an important part in the life of *ancient* civilizations. Even as late as the 14th, 15th and 16th centuries the alchemical system attained widespread favor, and, as in the ancient Egyptian temples, chemical laboratories were to be found in Christian monasteries.

The chemist in the past has been somewhat inclined, like his illustrious predecessor, the alchemist, to lock himself up in his laboratory and keep his secrets to himself. In more recent years, however, he has come out into the light of day and now presents the results of his studies before meetings of our Societies and publishes his results in our Journals.

Comment upon the retiring nature of the alchemists' successors, however, should not be taken in any sense as decrying the dispositions of our "fathers in chemistry" or deprecating their labors. None of us would think of criticizing the scientific habits of Boyle, Priestly, or Bertholet; of Liebig, Kekule, Pasteur, or of many of those who came after.

Many of these and other illustrious men did apply the results of their researches to practical ends and the Industrial Revolution caused many industries to establish chemical laboratories at their own works. It was not until the trade associations came into being, however, (particularly those forms of cooperative organization covering highly specialized fields) that capital may be said to have pooled its resources with chemical science, looking toward the establishment of a community of interests. Scientific Sections were organized and technical research instituted and the beginnings laid for studies that were later to advance both chemistry and commerce. Today there is hardly a university in the country but has its fundamental and applied research available for industry in the form of fellowships. For example, one well-known movement, sponsored by capital and initiated and administered by Professor Duncan first at the University of Kansas, later manifested itself in the establishment in 1911 of the Mellon Institute at the University of Pittsburgh with Dr. Duncan as the first director.

Fundamental Research Necessary for Progress

President Hoover, while Secretary of Commerce, in advocating and initiating the assembling of the $20,000,000 fund for research in pure science to be expended over a ten year period by the National Academy of Sciences, insured, in his characteristic, practical way, the continuation of industry's source of strength. The reservoirs of knowledge must not dry up. The streams and rivulets flowing into the power basin of Commerce must continue in volume. Fundamental research must go on and Chemistry while continuing its industrial cooperative program must not be neglectful of pure science.

Nevertheless, while fundamental research is necessary for further progress and while applied science must continue to be fostered, the resulting products of discoveries and inventions so made, must be distributed in order that those who wish may have the opportunity to get them. It would seem, therefore, that just as the second phase of the Industrial Revolution called for the more intensive services of chemistry, so today in still another phase of our industrial life, a new science has developed calling for a sympathetic understanding between Chemistry and Commerce, a mutual relationship between chemical production and distributive mediums. In chemical parlance, the relationship partakes of the nature of a "reversible reaction" in that the fortunes of the one are bound up with those of the other.

So the industrialist of vision establishes and maintains a department not only devoted to working out problems involving plant operations but also the coordination of

* An address delivered at Richmond, Virginia, May 2, 1930, before the Virginia Section of the American Chemical Society.

this department with other technical departments and with the development and sales organizations.

At the last New York meeting of the American Association for the Advancement of Science, Dr. Redman presented a very interesting study in which he discussed mortalities in the several stages of a product between the time of invention and the time of successful distribution. While one would not go so far as to say that all of these deaths could be averted, it seems reasonable to presume that economic research should diminish the casualties. Obsolescence, the price of progress, can certainly be met just as problems of supply and distribution are met and surmounted.

This necessity for a larger knowledge of economic conditions as they affect the chemical industry has evolved a new order of workers made up in large measure by those possessing both commercial and chemical training. It has introduced a new chemist classification.

Perhaps it may not be necessary for the chemical marketing specialist to have a chemical training, but basic knowledge of chemical science and its nomenclature should be extremely helpful in considering the fundamental aspects of chemical processes, the relation of one product to another, the possibilities for new and more efficient applications of them, as well as a more intelligent understanding of economic and commodity trends. Through these influences and trends, chemistry is recognized as basic to all industry, and *chemical* industry today exercises a profound influence upon the *political* economy of the world.

Economic Chemical Research

Economic trends or commodity tendencies may be caused by several factors among which may be noted: (1) the influence of other industries upon chemical evolution, and (2) the intrusion of synthetics into fields of use already occupied by natural products. To these factors of outstanding interest to the chemist may be added (3) those of availability of natural resources, and (4) waste and co-product utilization.

Consider how the automobile has affected chemical trends. It has caused a demand for more durable materials, for new and brighter colors, and new and better protective coatings. These latter have demanded solvents answering certain exacting specifications. The automobile industry is responsible for the development of anti-knock agents used as motor fuel constituents embracing a variety of substances useful for that purpose. Increased production of artificial leather followed the greater output of motor cars. This greater output was also reflected in a larger consumption of synthetic resins. Another industry that has affected the trend of certain chemical commodities is the rayon industry. Rayon—itself a group of chemical compounds—has exercised an influence over cellulose and the acids, both nitric and acetic. The demand for acetic acid for instance increased to such an extent that calcium acetate had to be imported to satisfy the demand for the raw material despite a continued growth in synthetic production as well.

Not so long ago the number of synthetics entering into competition with natural products was small but the rapid progress in chemical discovery adds new ones to the list almost daily. Ammonia, acetic acid, methanol, ethanol and the aromatics are just a few. Glycerine is confronted with glycol, and butyl alcohol faces internal dissension. Citric acid from fruits faces the constructive activities of the molds. The scene of natural camphor production will quite probably shift from the wild highlands of Formosa where live the head-hunting savages to more refined scenes of synthetic production.

Every state and territory in the Union is endowed with a wealth of natural resources—ranging from mineral deposits to forests and power sources. Abundant deposits of salt and gypsum, pyrites and sulphur, are to be found in certain localities; oil, coal, gas and limestone; clays, phosphate rock and bauxite in others. In short, our natural resources comprise practically everything to be found in a text-book on Economic Geology. The animal and vegetable kingdoms, likewise, to a great degree contribute a variety of materials which after processing finally enter into Commerce.

Utilization of waste and collateral products is constantly changing our ideas as to what are main products and what are by-products. Once, kerosene was the principal product of a petroleum refinery; now, the situation is reversed. Hydrochloric acid at one time was allowed to escape as a waste gas. Uses found for it soon made it a main product. The oils obtained from by-product coke ovens are today in as great demand as the residual product of distillation. Chemical history is replete with these reversals in relative economic importance of manufactured products.

Rise of American Chemical Industry

The consequent appearance of *new* products and the larger *application* of *both* old and new ones, has brought about a situation not comparable with that of any previous period in history. The incidence upon life of enormous quantities of materials having manifold uses must be characterized as truly great.

In the twenty-five year retrospect of the American Chemical Industry, recently issued by the Chemical Division at Washington, and in Professor Munroe's great work on chemical technology prepared for the Bureau of the Census in 1899, there are presented more than the mere chronology and statistics of the industry. Considering these along with the younger Silliman's contribution to American Chemistry, presented at the Northumberland celebration in 1874, it would be possible to write the history of American chemistry.

The magnitude and scope of chemical industry today is tremendous when compared with that of a hundred years ago, even indeed within the past *quarter* of a century. A comparison of the 1899 production figures with present day ones will afford an idea of how far we have traveled since that time.

Consider just a few outstanding examples:

	1899	1927	
Acetic Acid.....	400,000	5,500,000	(for sale)
Nitric Acid.....	1,500,000	3,500,000	"
Sulphuric Acid.....	7,300,000	43,000,000	"
Mixed Acids	1,100,000	3,800,000	"
All Sodas and Compound	11,600,000	114,000,000	"
Alums	2,400,000	9,500,000	"
Cyanides	1,600,000	6,300,000	"
Fertilizers	42,000,000	190,000,000	"
Paints and Varnishes	54,000,000	500,000,000	"
Explosives	17,000,000	72,500,000	"
Plastics	2,100,000	28,000,000	"

Sulphur, in the 1899 figures included pyrites, and production aggregated a value of $543,249. 1927 production of sulphur *alone* was valued at over $38,000,000.

Rayon, first exhibited at the Paris Exhibition in 1889, is now a firmly established industry, total United States production in 1927 amounting to $110,000,000.

Medicinal and toilet preparations, crude drugs, essential oils, waxes, matches, and a multitude of other commodities have also seen a remarkable development.

We cannot leave this discussion of the rise of the American chemical industry, however, without mentioning a branch constituting a key industry and occupying an important position in the chemical life of the nation—the synthetic organic chemical industry. In 1880, when the first mention was made in the Census returns of coal tar dyestuff manufacture, production amounted to 80,518 pounds of aniline dyestuffs. Expansion since the World War presents a magnificent record, preliminary figures for 1929 indicating the production of domestic dyes to have been approximately 110,200,000 pounds. Production of organic photographic chemicals totaled 581,000 pounds; synthetic flavors, 2,290,000 pounds; synthetic perfume materials, 1,596,000 pounds; synthetic phenolic resins, 31,471,000, and synthetic coal-tar medicinals, 5,000,000 pounds. An industry that can offer to purchase for a country, with one of its secret remedies, great areas in the tropics is not an industry to be neglected.

We have compared the present with the past in terms of production. A story of the expansion of our foreign trade would also read like a romance.

Today the world is our market place and we are sending to all parts of the globe, chemicals and allied products valued at over two hundred million dollars a year. On the other hand, our imports of materials for use in chemical and allied lines aggregate over 200 million dollars annually, two-thirds of which are either exotics or supplements to our inadequate domestic supplies requisite for the promotion of our industry.

The saturation point is not in sight. Production is limited only by human needs and desires and our economic horizons are constantly being pushed back in order to supply the rational cravings of teeming millions not yet acquainted with modern necessities, to say nothing of some of the luxuries.

Forward Movement not Geographically Restricted

The forward movement in American industry has been accelerated in recent years by a greater Southern participation. The creation of a New South, a new industrial South, has resulted from a recognition of its vast potential resources and the availability of cheaper power and new methods and lines of transportation. Other contributing factors are the supply of native labor, freedom for expansion and widening markets. This new state of affairs is reflected in a production value for all industries in the South in 1927 (the last census year) of $10,371,000,000, about one-sixth constituting chemicals and allied products.

The textile industry particularly has exhibited a southward movement and the processing of natural fibers and the manufacture of artificial ones—essentially chemical processes—has been an important development. The cheese industry since the practical eradication of the cattle tick has moved in a southerly direction. Coincident with these migrations there has been the establishment of other new industries. Expansion of old ones is reflected in the carbon black and the naval stores industries; and to the vegetable oil industry has now been added tung oil. Finally to supplement increased phosphate rock production we have another fertilizer material—fixed nitrogen—added to the South's list of products. Carbon bisulphide is expanding, diphenyl is no longer a laboratory curiosity, and cotton weed bran, the lowly peanut-hull, and the Jerusalem artichoke will probably be converted into xylose on a commercial scale.

Enterprise in Virginia

Statistical data for the South in general and Virginia in particular have been so admirably presented by Dr. Hitchcock, that it is unnecessary here to more than mention the leading position occupied by Virginia in the production of chemical and allied products and to note some opportunities worthy of consideration.

"Down Where the South Begins", here in Virginia, you have entered into a new age. Already known as the "Mother of Industry on the American Continent", the State in which "were established the first salt plant, the first glass works, the first leather tannery", you now have added another type of "first", first in production of rayon. You will also, it is said, soon be able to guarantee United States independence of foreign nitrogen.

In 1927, the value of all products manufactured in Virginia aggregated $671,000,000, a 14 per cent increase over the total 1925 value. Of the 1927 value, chemical and allied products aggregated $129,000,000, divided into 20 groups, illustrating the diverse nature of Virginia enterprise.

At the same time, what has been done represents only a portion of what may be accomplished. A booklet recently issued by the Virginia State Chamber of Commerce impresses one with the great potentialities awaiting development. Water and rail serve not only a section that may be glimpsed from the deck of any steamer com-

ing down the Bay or in through the Capes but a vast territory to the north, west and south, as well.

Hampton Roads Port is a natural gate of ingress to the West and South, and it is one through which a steadily increasing outflow of all sorts of materials will find their way to foreign fields. The Hampton Roads Port is especially favored by its location and the nearness to the East and West coasts of South America and by the territory which it is capable of serving. Mutual requirements of this area and the United States should ensure cargoes coming and going.

In the export studies included in the traffic survey previously mentioned is one on coal and the thought occurs that some could be processed in ovens and the by-products utilized. Coke production could mean a metallurgical industry and an increased tar production could mean more road materials and more domestic creosote with a short haul and perhaps an expanded creosoting industry. The manufacture of other products ranging from crudes to finished products, from motor fuel constituents to dyestuffs, is not incapable of consideration. The import study on cacao beans suggests theobromine and caffein, this thought in turn suggesting the field of fine chemicals. The molasses study suggests not only industrial alcohol but also images the booming solvents industry. Reflection upon the pork and pork products study visualizes slaughtering and packing house activities, with consequent production of biologicals, soaps and glycerine.

In addition to these suggested lines of chemical endeavor may be added casein, not only to supply the coated paper industry, but also as a basis for the casein plastics now finding wide application.

Continued Progress of Chemical Industry Necessary

Suggestions such as the few just given inadequately present our possibilities. They seem so very meagre. Could we but transport ourselves into the future—let us say to 1950—we should, no doubt, be amazed at what had transpired in the intervening score of years.

The historical glance *backward* has shown us the great forward strides made since earlier times by American Chemistry. We are quite aware too that scientific discovery and invention are proceeding at an ever-increasing rate and in the light of history, our progress in the future is to be more rapid than in the past.

The functions then, of *chemistry-in-the-future,* must be more comprehensive than at present and must certainly embrace an understanding of its economic importance. The service of chemistry must be not only in the discovery and the application of scientific and technological facts but chemistry must also serve by solving the larger problems of distribution in its broadest sense. We must lay more emphasis upon the *commerce* of chemistry, upon the economical distribution of chemical wares. New uses must be found for old products, old industries may justify expansion, and new ones would logically be inaugurated if deemed advisable.

It is not enough to visualize the great potential awaiting development—to view the perspective—and stop at that. Practical and efficient *methods* for bringing about the desired ends must be formulated and, happily, chemical industry itself, as well as Governmental institutions, have made a beginning along this line.

A general method of approach, capable of specific application, of arriving at a program of effort, is through the *chemical-economic survey.* Such a survey when completed, should show fairly conclusively whether or not a given material shall go into production, how long an industry can continue its current program, whether it should switch immediately or gradually, or whether it should pick up and move to some other part of the country.

In building the survey structure the technique to be followed will, of course, depend upon the problem at hand, but no matter what the survey, whether of some particular branch of industry or of some particular commodity or group within the industry, the foundation upon which the superstructure is to be raised must consist of immediate, reliable, adequate and permanent records.

Bureau and Division Aids

The Department of Commerce, because of its relation to other Government establishments and to industry, has at hand or can point the way to the many sources of information so important in determining the position or status of a specific chemical industry or commodity, or in determining their trends. Cooperation in this respect is gladly accorded through the Chemical Division of the Bureau of Foreign and Domestic Commerce, which, established eight years ago by Mr. Hoover when he was Secretary of Commerce with Mr. Concannon as Chief, endeavors to render practical service in the application of commerce to chemistry.

Nearly every day, one or more interesting problems are presented. Someone may ask—"How are the solvents?" or "What is the future of acetic acid and how?" Or the question may be "Where and in what quantities can rotenone-containing plants be found? Has it been synthesized yet?"

The functions of the Division are essentially trade promotive and do not include any of a regulatory nature. Through regional surveys and immediate services available in 58 American cities the Bureau assists domestic commerce. To promote foreign commerce the Bureau also has available the services of its 56 offices abroad and the collaboration of the consular service.

The information thus made available covers a multitude of points: Magnitude of the situation as affected by foreign competitors; climatic conditions; advertising; make-up and habits of the population; purchasing power; chemicals and allied products manufactured locally, or other sources of supply. Questions related to transportation facilities, customs tariffs and internal regulations affecting the importation of sale of American products in over-sea countries are looked into and reported upon.

In addition, the Bureau maintains lists of prospective agents in each country and keeps a complete commercial report on each one for the confidential use of American

firms. Up-to-date information is not only given regarding trade conditions, but each week the Bureau publishes a number of "Trade Opportunities" which are inquiries from parties with a definite interest in buying who wish to get in touch with manufacturers here.

A thousand men are at your service in the four corners of the world to gather together data bearing directly upon foreign trade promotion and at the Washington *headquarters* and the district and cooperative offices throughout the country you will find the Department's facilities at your disposal.

Meeting of Preliminary Directorate of U. S. Institute for Textile Research

REPRESENTATIVES of the textile industry met at the Chemists' Club, New York City, on Tuesday, July 29th, to set up a temporary organization which is to function until the United States Institute for Textile Research can be given more permanent form at the meeting for the entire membership which is to be held November 6th.

With the election of P. J. Wood of the Oriental Silk Printing Company as acting president and the adoption of a tentative code of by-laws, the preliminary organization, which will carry on the work of expanding and consolidating the membership, was well started. Other officers to serve until the November meeting are as follows: 1st vice-president, E. N. Hood, treasurer, Pequot Mills, Salem, Mass.; 2nd vice-president, Thomas T. Clark, treasurer, Talbot Mills, Billerica, Mass.; treasurer, Dr. E. H. Killheffer, president, Newport Chemical Works, Passaic, N. J.; secretary, Charles H. Clark, Boston, Mass.

The following were appointed members of the acting executive committee: P. J. Wood, acting president, *ex-officio*, Dr. E. H. Killheffer, E. N. Hood, Thomas T. Clark, E. A. Clements, president, Globe Knitting Works, Grand Rapids, Mich.; C. E. Emerson, vice-president, Robert & Co., Atlanta, Ga., and W. C. Taylor, secretary-treasurer, Southern Textile Association, Charlotte, N. C.

The research committee was elected by the executive committee to provide for the development of a definite program of fundamental research with the following personnel: Dr. W. E. Emley, Bureau of Standards, Washington, D. C.; George H. Johnson, research director, Laundryowners' National Association; Dr. W. F. Edwards, director of laboratories, United States Testing Co., Inc., New York; Prof. Louis A. Olney, Lowell Textile Institute, Lowell, Mass.; Prof. George B. Haven, Mass. Institute of Technology, Cambridge, Mass.; E. N. Hood, treasurer, Pequot Mills, Salem, Mass.; C. E. Emerson, vice-president, Robert & Co., Atlanta, Ga., and Louis A. Hird, treasurer, Samuel Hird & Sons, Inc., Passaic, N. J. This committee is to report back to the executive committee before September 15 and its recommendations will be made available to the directors of the Textile Foundation. This latter body has already received the Institute's request for a hearing in support of the suggestion that the Foundation fund be kept intact and only the income appropriated for research.

The by-laws provide for twenty-four directors, divided into three classes of eight each, one class being elected for one year, another for two and the third for three years. The executive committee is similarly divided into three classes of two members each. It is the hope of these preliminary groups to attract leading men of the industry who will be fully representative of its major branches, to become members. Six types of membership in the Institute are provided: founder members, benefactor members, sustaining members, life members, contributing members, and annual members. An important feature is that only two classes paying annual dues of $10 and $100 contribute to current funds. The fees received from the other four classes become a part of the permanent funds, administered by the trustees, and it is hoped that in time these funds will become large enough to finance through their interest, research upon an adequate and permanent basis.

Also included in the by-laws is a provision for the selection of a self-perpetuating board of trustees. "The Board of Trustees shall have the custody and management of the permanent funds and securities of the corporation, and shall have general charge of such investments, and it shall care for and invest all funds and property constituting such permanent funds, and shall dispose of the same at its discretion for the purpose of permanent fund reinvestment. It may hold as investments any securities in money or property given, assigned, transferred, devised or bequeathed to the corporation, and retain such investments in the same form as when so given; and it may invest any such funds from time to time in such securities and in such form and manner as may be permitted to trustees, or to charitable, benevolent, or educational corporations, according to the laws of the State of New York, or in such securities or property as may be authorized by any such gift, transfer, assignment, devise or bequest. All securities or other property of such form as to permit of such treatment shall be kept by it in a vault or safe deposit box in such bank or trust company as may be approved by the Board of Trustees."

Regarding the establishment of permanent and current funds, the code of by-laws provides: "All the funds, securities and property of the corporation, except such as shall be derived from payment of annual dues of the annual and contributing members, and from income upon investments, and from gifts, donations, devises, or bequests, manifestly of a character not intended to become a part of the permanent funds and securities, shall constitute the permanent fund as distinguished from current funds."

Textile specialties in Great Britain, France and Germany are being investigated by Walter Meyers of the American Aniline & Extract Company of Philadelphia, who is touring Europe for this purpose. Mr. Meyers' mission is to negotiate for the purchase of American rights to new products and processes that can be used to advantage in this country. It is stated that should Mr. Meyers' quest be successful, the American Aniline & Extract Company will offer the new lines in the early fall.

AMERICAN DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

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Published biweekly by
HOWES PUBLISHING CO., INC.
440 Fourth Avenue, New York City

A. P. HOWES, President

Subscription price $5.00 per year; Canadian $5.50; foreign $6.00

Vol. XIX August 4, 1930 No. 13

WHY CHEMISTRY?

THE day of the old-time dyer is past. No longer are rule of thumb methods followed; no longer is dyeing a family affair handed down from generation to generation. Today the dyer, besides being an artist, should be a man with a very extensive knowledge of chemistry.

In this age of increasing competition, the dyer, in order to qualify, must be able to keep the cost of dyeing down to a minimum and still turn out work that is satisfactory. In the years long gone, dyeing was done in the most simple manner. The main object, of course, was to color the fiber, the results so far as durability were concerned, being secondary. Cost in those days was a minor consideration. When dye houses were established, they were, as a rule, assured of a market, and the fulfilling of market needs was their function. There were only comparatively few dyes to choose from and those were more or less standardized so far as application was concerned.

At the present time there are approximately two thousand dyes belonging to about thirty chemical groups. The dyes in each of these groups have certain peculiar characteristics. The dyer by being familiar with their chemical reactions can reason out, therefore, how any particular dye is likely to act under certain conditions. The advantages of this may easily be seen. The chemist would know just why a particular ingredient was used in the dyebath; but, in case that ingredient were not on hand, he would not have to stop production, for he could substitute something else in its place which would have the same effect.

Again, it is often true that in dyeing various materials the procedure must be altered. The practical chemist knows not only how but why it should be altered, and thus he is able to meet any emergencies. Oftentimes a knowledge of chemistry makes possible the use of less costly materials in dyeing: for example, potassium bi-chromate was used for years in the dyeing operations, and it was not until the chemist with his "why" came along that the cheaper sodium bi-chromate was substituted for it. The dyer having a knowledge of chemistry should not be dismayed by any such problems as: hardness of the water in dyeings run at various times, dye not soluble, some material out of stock, certain classes of dyes difficult to strip, uneven dyeings and so many other problems that it would take a book to enumerate them.

A knowledge of textile chemistry enables the dyer to trace faults in the finished fabric to their origin. Formerly, if finished goods were uneven or tendered, the blame was invariably placed on the dyer. By having a full knowledge of the chemistry of the finishing operations, the dyer now is able to show that the cloth was tendered there, and he could show, too, whether unevenness was due to too much soap being used in the fulling mill.

Chemistry develops inductive and deductive reasoning, it stimulates the imagination and furnishes training in observation, judgment and mental discipline. The dyer with these qualities developed is a very valuable asset to any company. He would not be a mere employee, but a man interested in having his department function in the most efficient manner. His knowledge would permit the most effective utilization of the property with which he had to work.

AS TO FINANCING RESEARCH

NEARLY everyone connected with the dye industry is in favor of research. To date, the difficulty with respect to co-ordinating, and, so, advancing of research in the broad sense, has been one of finance. A few men can not be expected to use their capital in order that all may benefit, for it is not human nature to do things in that way. As a matter of fact, the problem of finance in this special matter is not merely how to get enough money for the required purposes; it is how to obtain the money in such a manner that each one who is benefited pays his full share.

It can only be through perseverence and through studying all possibilities that a satisfactory conclusion may be reached. The Wool Industries Research Association in England has, until now, been confronted with the problem of finding adequate funds with which to carry out their research program. The British Department of Scientific and Industrial Research recently offered the Association £10,000 per annum providing they should raise an additional £20,000 a year.

Upon this offer, the British Association devised and approved a plan whereby a levy or tax of a certain amount is made on all imported wool consumed in the country, and a corresponding levy on employers proportioned to the number of their operators. These taxes are very nominal, and yet it is estimated that they will yield a total of more than £30,000 each year. This system will

give the British organization sufficient funds with which to work, and each member will pay for the research operations according to the size of his business. It also might be well to say that a method for collection has been devised which the Association believes will be successful.

The problem which confronted the English Wool Industries Research Association is closely parallel to that confronting our United States Institute for Textile Research. The Institute is at present in a favorable position to secure financial help from the Textile Foundation. Without doubt, such help would need further augmenting, and this might best be accomplished by studying what the Wool Research Association has worked out, and devising an appropriate plan, to which lessons learned from the English procedure might possibly contribute.

When one considers the number of companies that are represented directly or indirectly in the Institute, he readily can see that it would require but a relatively small contribution from each for an adequate research program to be maintained.

A WORD ON ODOR

A STORY is told of a silverware manufacturer who found that his business was going in the wrong direction because the boxes in which he packed his goods had an unpleasant odor. The glue used in the manufacture of the boxes became distinctly disagreeable after standing in the shop. With the removal of this "jinx" an impetus was given to sales—and profits.

Leather, cardboard, wood, rubber and a long list of other materials, including furs, wrappings and cloth are none the better for queer olfactory properties. Sometimes manufacturers are slow to see that odors help or detract from selling qualities. Many of them might take a lesson from the silverware manufacturer. Cloth is one of the most widely distributed of commodities and yet up to the present very little has been done to increase the sales appeal as far as odor is concerned.

Advanced marketing methods demand that everything possible be done to make the goods more acceptable to the consumer. There is no doubt that improvement may be brought about in the odor of many fabrics. Unpleasant odors are caused by such things as rancid soap in scouring or fulling, singeing, or even sometimes from certain methods of dyeing. Not a few of these odors may be eliminated at their source; the others may be taken care of by the use of suitable aromatic compounds. Many times, even though a fabric is not distinctly disagreeable in odor, the odor may be improved, giving the goods just that much more sales appeal.

The Publicity Bureau of the Merchants' Association of New York have recently published a booklet entitled "New York — America's Style and Buying Center." Copies of this booklet are now being distributed by the 7,500 business houses constituting the membership of the Association. It calls attention to the large production of textiles in the city and the great facilities afforded as a merchandising center.

The Inside Dope of Making Textiles Smell Good

By Dr. Donald A. Laird
Colgate University, Hamilton, N. Y.

WITH the textile industry giving greater attention than ever before to turning out a product that has a good smell rather than the age-old musty clothy smell the advice of the outstanding specialist in this field should be of considerable helpfulness.

How to turn out a piece of goods that not only feels quality but also smells quality is the question. Some have doubled their washings, overlooking that a blue, black, or brown dye which usually yields a smell distasteful to the consumer cannot be rinsed out. Others have tried perfuming, only to find that it is expensive, uncertain, and that after all women are finicky about perfumes although they agree on a good, clean, quality smell.

Finishing pastes and oils are the crucial elements in the undesirable smell of the fabric, in addition to dyes, says Dr. Eric C. Kunz of Montclair, N. J., who has been engaged in this work successfully for more textile firms than any other individual chemist.

"The finishing pastes," he reports, "are usually little more than special soaps which give the goods a soft, smooth touch after dyeing. Naturally, soaps get more or less rancid under various conditions over which the manufacturer has no control after goods leave the finishing mill.

"Soap manufacturers have known this for years, and even unperfumed toilet soap or laundry soap contains a small amount of industrial aromatics to cover the rancid smell the soap is likely to acquire otherwise before being used. Laundry soap usually contains from two or four pounds of odoriferous aromatic chemicals per thousand pounds of soap to cover—and as we shall see, to prevent—rancidity.

"A somewhat newer development in textile finishing is the use of a mixture of vegetable and mineral oils. These, like the soaps, have their own oily smell which is not pleasant, and in addition may become rancid, or go sour.

"Finishing oils or pastes which do not use aromatics are years behind the prosaic laundry soap industry. It is not usually rinsing that is crucial, but the oils and pastes. This is especially true of silks. In some cotton goods the trouble is found in the starch breaking down.

"Actual factory experimentation has disclosed suitable aromatics for use in either condition, and we now have discovered aromatics which can be used in the starches and which will withstand the heat of ironing so that the goods go across the counter with a good smell.

"Recently, for instance, a manufacturer of finishing pastes complained that from time to time his pastes started to become rancid before the customer used them. To overcome this he added 1% of carbolic acid. This stopped the tendency to become rancid, but it imparted the odor of carbolic acid which was not desirable. During two months' experimentation it was found that some industrial aromatics, used in only half the concentration of the car-

bolic acid, would also stop the tendency to become rancid, and at the same time imparted to the products an agreeable, clean odor. Many industrial aromatics have more germicidal power than carbolic acid, and do not yield the unpleasant smell.

"It is always wisest to get at sources of unpleasant odors, rather than simply to try mask the odor that is harming sales. Simply killing an odor can be done by using a stronger odor, but in that case the unpleasant odor is not neutralized. What we are now doing is to make the offensive smell a part of the good odor; in other words, we are putting the bad odor to work rather than trying to remove it.

"Take the case of artificial leather which normally has a very strong odor of linseed oil. We have tested some thirty aromatics recently which were incorporated into the raw materials. Four of these blended with the linseed oil odor to make the distasteful odor pleasant when the aromatics were only 1/10 of 1% of the weight of the finished piece. The other aromatics, which did not blend with the linseed odor, had to be used in large amounts, or until they were intense enough to smell stronger than the oil itself.

"The four, however, blended with the oil smell to produce a good smell, just as the foulest imaginable smells are basic in producing a jasmine perfume. This is the general principle now being followed: Don't try to kill the smell that is a sales hazard—put it to work by blending it with aromatics to produce a smell with sales appeal.

"Packing textile products with a sachet powder, or with a washing slip which is perfumed is merely a compromise solution. It is also more expensive than re-odorizing and assuring a good salable smell at the source. These novelties may give some temporary advantage over competition, but it is doubtful if they will be able to compete in the long run with a basic treatment which builds a good smell into the product itself. Some manufacturers report to me, in fact, that the ultimate consumer is suspicious that the piece packed with sachet is trying to cover up defects in manufacture, whereas a piece re-odorized at the source is immediately recognized as having quality built right in."

Dr. Kunz's comments should be taken seriously by the textile industry. There is more activity toward re-odorization taking place within textile plants than those who have not been keeping in close touch would realize. An observer-who-happened-to-know, for instance, was in a wholesale textile house in New York when one of the proprietors commented that the pieces they were now receiving from one convertor marked a new triumph in quality. The wholesaler did not know that the impression of a new level of quality came from finishing pastes which had been treated with aromatics. The observer happened to know this, but said nothing. There are a good many in the industry who are saying nothing, but who know a great deal about reodorizing.

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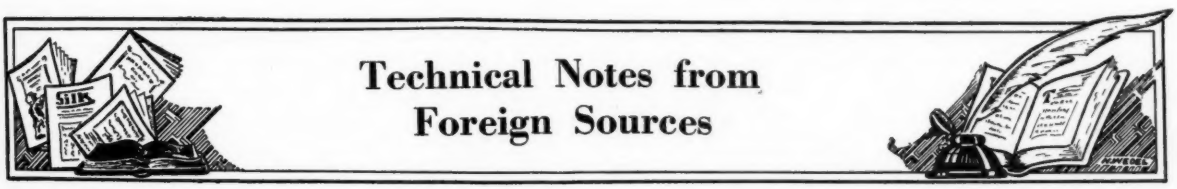

Photochemical Decomposition of Simple Azo-Dyestuffs

Prof. R. Haller and Dr. G. Ziersch—Mell. Textil-Ber. 10,951 (1929).—The authors have carried out a careful investigation, from a chemical standpoint, of the changes of degradative nature brought about by strong and persistent exposure, to light, of a series of typical azo dyestuffs. It has already been found that indigo dyed upon cotton is oxidized to isatine by insolation (the technical term for long exposure to sunlight), and the idea of the author was that, by choosing suitable dyestuffs, the end-products of decomposition by light might be definitely identified, and so some idea might be gained about the nature of the process which insolation involves. As the largest number of important dyestuffs belong to the azo group, and as no definite information as to the nature of the effect of light upon these dyestuffs was extant, it was this group which was chosen; and, since it was to be expected that the reactions involved in this degradation by light would be of a complicated sort, it seemed best to employ such azo dyestuffs as were as free as possible from unnecessary substituting groups. For this reason, insoluble or pigment colors, which possess the simplest composition, and which could easily be produced upon the fiber, were chosen. To be precise, beta-naphthol was the second component selected, and to it were coupled the diazo-compounds of aniline, o-toluidine, m-xylidine, o-anisidine, alpha-naphthylamine, m-nitro-aniline, p-nitro-aniline, and m-nitro-o-anisidine. The pigments thus produced were developed upon cotton fabric, and the swatches examined under insolation. Also, the pigments in substance were prepared and purified (a table of their melting-points and external characteristics, etc., is given). The pigments of this group would be peculiarly appropriate for the study in question, since they can be produced in quite pure form on the fiber, and are also decidedly sensitive to light.

In regard to the source of light, since the question was really that of daylight, it appeared that the propriety of using any artificial light-source was hardly to be thought of. The quartz-mercury-arc was out of the question, since its spectrum is very different from that of sunlight. An

Osram point-light, also seriously considered, possesses too short a life, nor is the intensity of its radiation sufficiently high. The source tested most carefully was one of the new glow-lamps with a bulb of Uviol glass—an Osram-Uviol lamp (500 watts, 220 volts). The results obtained with it were disappointing—in fact, more than that, as after 500 hours no alteration was visible on the swatches exposed. There was trouble also from heat-radiation; in the case of the simpler pigments, the latter sublimed to a considerable degree from the inner part of the fabric to the surface, and formed a sort of protective coating against the light. It was finally found that there was no escape from the use of daylight irradiation, though in some of the work the Fade-Ometer was employed. The measurement of the light-intensity was carried out with the Victoria Blue-paper method of Krais.

Through some special tests carried out with standard light-filters (Schott's), it was found that the rays which exerted the destructive action upon the pigments were of a wave-length of 500 to 300 Angst., and (as would be expected) in the green to violet region of the spectrum. It was therefore evident that irradiation could successfully be carried out under protection of glass, without fear that this would absorb the rays whose action was desired. The same fact has been found to hold good for Naphthol AS pigments. No glass covering, however, was used in the tests.

In exposure of the swatches to daylight, since the purpose was to attain maximum destruction of the dyestuff, the material was insolated on each side for the given number of light-hours. The usual phenomena were observed —lightening of tone, dulling of brilliance, fading, and bleaching out, in the usual sequence. In every case, when the color of the pigment was gone, a dirty-yellow residual color was observed to have been assumed by the fabric. Beside the tests upon fabric, the same tests were carried out upon the pigments in substance, as precipitated upon an inert substratum of barium sulphate, and spread upon plates. Such samples proved more resistant to light than those upon fabric. Further, the pure pigments were insolated in the form of solution in glacial acetic acid, inclosed in sealed glass tubes. These solutions behaved as did the swatches; the liquids finally assumed a dirty-yellow color, with the deposition of a slight amount of a brown precipitate. Opening of the tubes showed pressure to exist.

An interesting series of experiments was also carried out through the irradiation of dyed swatches inclosed in glass tubes, which were filled with gases other than air, viz., ozonized air of about 12% ozone, oxygen, nitrogen, hydrogen, and carbon monoxide. The light-source in this series of experiments was the Fade-Ometer arc. Similarly prepared swatches (i.e., sealed in gas-filled tubes as before) were kept in the dark for the same length of time, for comparison. After exposure of the set, the gaseous contents of both sets were analyzed. The results showed oxidation to have taken place (CO_2 being formed). The irradiated tubes, containing hydrogen and nitrogen as an atmosphere, also gave some CO_2, showing that the method of filling the tubes with gas was not as effective as it should have been. Undyed cotton so exposed also yielded CO_2. It was found that the amount of CO_2 formed was dependent upon the concentration of oxygen present in the atmosphere of the tube. Scharwin's work has indicated that CO_2 formation in the irradiation of cellulose is connected with the formation of oxy-cellulose, and the authors' work has confirmed this (dyeing of exposed samples with Methylene Blue, and determining the amount of dyestuff taken up).

The dyed samples in the above inclosed tests gave more CO_2 than did undyed cotton, indicating that in this case the dyestuff also must enter the oxidation-circle. Also, some nitrogen was liberated, pointing to a partial disruption of the N-N group.

A considerable amount of work had already been done upon the oxidation of azo-compounds, using red, fuming nitric acid, perhydrol, chromic acid, lead peroxide and sulphuric acid, and electro-chemically, with varying results. The authors therefore oxidized the pigments in question according to the second of these methods (that of Angeli, using perhydrol) as being apparently best adapted to the present circumstances. Results were none too illuminating: phthalic and phthalonic acids were detected definitely among the products obtained, indicating rupture of the naphthalene ring, but little else beside complex phenolic substances could be isolated. The irradiated samples on cotton, however, yielded yellow substances which were proved to be beta-naphtho-quinone, and also phthalic and phthalonic acids, which clearly were the result of further oxidation of the naphthoquinone previously formed in the breaking-down of the dyestuff. The extracted fabrics (which always came out of a dirty-yellow color) also yielded with caustic alkali what was apparently a hydroxylated ring compound (it dissolved from the fiber easily with caustic), whose identity could not be established. The reason for supposing it to be of a considerable molecular weight (polymerization?) lay in the fact that when diazotized amines coupled to it, only such amines as p-nitro-aniline (well-known as one of the most vigorously-coupling bases, and therefore resorted to in case of second components which couple reluctantly) would so react.

The whole paper, of which the foregoing is a decidedly brief summary, is a carefully worked-out study, such as we always look for from Prof. Haller and his co-workers.

Fat-Solvents in Washing

Dr. R. Blaser—Mell. Textil-Ber. 10, 963 (1929).—Fat and oil-solvents, kier-oils, etc., have been frequently mentioned in the textile literature, and usually in a favorable way; but at present their value in certain processes at least, is much in question. These solvent-compounds consist mostly of soaps in mixture with organic solvents such as benzine, xylene, trichlorethylene, carbon tetrachloride, hexaline, methyl-hexaline, etc. When such preparations are dissolved in water, the soap or other

emulsifying agent emulsifies the solvent constituent, and then usually forms a milky emulsion, sometimes a clear solution. The expression "solubilized benzine", etc., is sometimes used technically in such a case. The assumption has prevailed, that the organic solvent in question, finally divided in the soap-solution, will dissolve the oily or fatty material to be removed, and so greatly facilitate the cleansing of the fabric which has been spotted or smeared with the oily contaminant. As such an assumption appears at first sight to be well founded, its plausibility may be the reason why careful experimental work upon such mixtures has rarely, if ever, been carried out. The favorable impression expressed regarding such mixtures has been simply an expression of what it is thought ought to be the case, arguing from the merely chemical composition of the mixtures. But such statements, made as actual claims, cannot really be substantiated.

Solution of oily smears upon a fabric can take place only when there is actual physical contact, wetting, between the smear and the solvent. This condition is hardly met with in most cases, and further, the product used is employed at so high a dilution that any visible result is hardly possible. An actually active solvent loses greatly in solvent power when it is emulsified, as can be seen by a simple experiment; a spot of tar upon a piece of cotton cloth almost entirely disappears when treated with benzine, and likewise when treated with one of these fat-solvent preparations (50% hydrocarbon), if they are applied to the dry fabric. But, if the piece of fabric is first wetted out in warm water and then treated with the preparation, the complete removal of the spot is not possible, in spite of long rubbing. The emulsified solvent works poorly.

These compounds are used in washing by hand, for removal of spots of mineral oils. Their superiority in this application, to common soap, is unquestioned. They are also frequently added to wash-liquors in the case of unusually dirty material, and oily outer garments, such as machinists' overalls, etc. Whether they are of any special use in such cases is more questionable.

The author has carried out some experiments intended to check up on the actual value of these compounds. He impregnated a swatch of cotton cloth with a known weight of machine oil, and after three days sewed the swatch loosely upon another piece of cotton cloth, and subjected the union-swatch to washing in the apparatus usually employed in laundry establishments. The oil which remained unremoved was estimated by comparison of the swatch with standards in ultra-violet light (see Blaser and Girsberger, Mell. Textil-Ber. p. 680, ser. 1928). This method permits of rapid and accurate estimation after the standard scale has been established. The same experiment was carried out using pure paraffin oil of sp. gr. 0.86, a substance which is more difficultly emulsifiable and so more difficultly washed out. The paraffin oil was first made capable of luminescing plainly in ultra-violet light by dissolving in it a little resin. In all the experiments, little difference could be noted between the action of common soap and of a bath containing the detergent compounds under consideration. The oil-spots were still visible, though of course fainter; the swatches could not be claimed to have been washed clean.

Similarly, Kind's (Mell. Textil-Ber. p. 1024, ser. 1927) work upon kier-oils has proved that the use of such oils does not produce better whites than does the common kier-boiling. Many practical men feel otherwise about it, but likewise many others consider that such compounds are really of no use.

The author also considered the converse case. When an oil-smeared fabric is boiled with a scouring-bath to remove the oil, the clean, or the cleaned parts of the fabric may of course take up the oil which has been removed from the dirty part of the fabric and is floating about in the bath in the emulsified form, particularly, of course, if the fabric has been very oily indeed. His work shows that such is actually the case, but that here the presence in the bath of one of these detergent compounds does to a slight extent keep the oily matter from going back upon the clean material—to a slight extent, to be sure, he observes.

One last pertinent observation is made, whose meaning we fear would be overlooked by many unless it were specifically pointed out; the poor emulsifying power of these special baths is shown by the fact that when specially oily material, such as oily, greasy overalls, is washed in the usual laundry machinery, the interior of the machines becomes coated with the oil removed from the material. If the emulsifying power of such baths were as great as were to be desired, the oily extract would be kept in suspension in the bath, and could not separate out except on long quiet standing. The fact is always noticed, its significance is usually overlooked.

Lilienfeld Silk—An Advance

Dr. Roos—Kunst-Seide 12, 86 (1930)—The goal of the viscose-silk industry, of late years, has been the production of finer and yet much tougher fibers, such as could compete successfully with the finest tension-spun cupro-silks. The cost of producing such fibers, if such fibers could be produced, would also have to be as low as that of the older viscose-fibers of greater diameter. Much work has been done upon the problem in two directions; one, the Agfa-Travis method, which is not in question here, and the other the Lilienfeld method. The latter process appeared at first to be a decided step forward in the artificial silk industry, but as yet it has not apparently been much developed, although Glanzstoff has acquired the rights to its development and commercial utilization. The process itself is embodied in British Patents Nos. 212,865, 274,521 and 281,351-52, and consists essentially in treating alkali-cellulose at temperatures not over 2° C., best at —3° to —15° C., with carbon disulphide. By employing a low temperature for the reaction of the carbon disulphide upon the alkali-cellulose, the time factor is decreased, the cellulose is less degraded, and the ripening-process can be omitted. The quantity of carbon disulphide

can be cut down to 1-6 to 1-10 mol. for 1 mol. of cellulose. The viscose solution produced is colorless, can be kept well, and does not give a milky, cloudy product on coagulation. It appears that the conditions of preparation must greatly hinder the formation of the long chain-structure which cellulose may, as is at present believed, take on.

The first step in the Lilienfeld process then, is the maintenance of an unusually low temperature in the viscose synthesis. The second step consists in a development of the spinning process by use of a precipitating-bath of sulphuric acid of about 50-70% (Brit. Pat. No. 274,521). This patent prescribes a sulphuric acid strength of not less than 55%, preferably 65-68%, and recommends spinning under tension. It is pointed out that the usual ripening-process is not requisite, and that the shortening or total omission of ripening is really preferable. In ripened alkali-cellulose the cellulose-content should be brought to 8-12%, and the amount of carbon disulphide should be greater than 40% of the weight of the cellulose. The strength of the acid to be used depends upon the degree of ripening of the alkali-cellulose, the time of ripening of the viscose, the properties of the cellulose-material source, the viscosity and the cellulose content of the viscose. In general, viscose ripened for a longer time demands a weaker acid which can be used at ordinary temperatures, or below or above room-temperature. The length of the spun fiber during immersion after spinning can vary from 3 to 60 cm., or even up to 100-200 cm. With stronger acid a shorter immersion is best, and the time of immersion most suitable depends upon the temperature of the bath. The bath may contain mineral acids, sulphates, sulphites, nitrites, boric acid, glycerol, glucose, alcohol, salts of organic bases, or organic acids.

A close study of the above, and comparison of the details with those of many other patents, suggests that the L. process really offers nothing strikingly new.

A complete summary of a considerable number of patents of various sources is added, all indicating the author's viewpoint, that it is therefore no wonder that the Lilienfeld-process silk possesses a relatively high tensile strength in the wet as well as dry condition, but that its elasticity is the poorest possessed by any kind of artificial fiber. Even this last characteristic is of striking importance for the working up of such a fiber. Further, its repulsive action toward water makes it hard to dye evenly, or sometimes to dye it at all in the right sense of the word. The use of such high concentrations of sulphuric acid in the spinning-bath too, occasions serious technical difficulties, as well as danger to the health of the workmen employed.

The author concludes that, if these difficulties can be overcome, there is undoubtedly a future for the process; but at present, there prevails about it a significant silence.

Action of Light Upon Cotton Dyed with Certain Vat-Dyestuffs

F. Scholefield and E. H. Goodyear—Mell. Textil-Ber. 10,867 (1929)—Scholefield and Patel have already pointed out certain peculiar phenomena as occurring when yellow or orange vat dyestuffs are dyed upon cotton; these points can be summarized as follows:

1—Yellow and orange vat dyeings upon cotton are much more sensitive toward the effect of light in tendering the fiber than are dyeings with vats of other colors, especially blues and violets.

2—With mixtures of yellow or orange vat dyestuffs on cotton with blues or violets, the light-fastness of the blue component is generally decreased through the presence of the yellow component.

3—The fiber is weakened during the process of dyeing with yellow or orange dyestuffs if the material impregnated with the vat is exposed to light and air; if a second dyestuff, e.g., Ciba Blue 2B, is also present, this latter may be partly or wholly destroyed.

Landolt investigated the subject further, and made a number of highly interesting observations. For example, tendering takes place if cotton dyed with Anthrene Yellow GC or Ciba Yellow G is wetted with caustic soda solution and exposed to light. He does not consider that the process of dyeing has itself anything to do with the tendering, and therefore, that formation of hydrogen peroxide by auto-oxidation of the vat is not the cause of formation of oxycellulose. He has rather made it clear that the vat dyestuff, under the influence of light, in the presence of caustic soda, brings about this formation of hydrogen peroxide, and that this substance acts as a carrier for atmospheric oxygen in the formation of oxycellulose, the cause of tendering; he has also shown that water must be present, obviously, for the production of the peroxide. In absence of light the peroxide was not formed; and a very short exposure to light is enough to initiate the generation of peroxide and subsequent tendering from the formation of oxycellulose. Scholefield himself has already observed that the presence of caustic alone in mercerized and incompletely washed cotton is enough to bring about oxycellulose formation when the goods are exposed to light.

If Landolt's view of the action of light upon cotton during the dyeing with e.g., Cibanone Orange R is correct, then the extent of formation of oxycellulose must be the same as that when cotton, wet in one sample with caustic, and in another with caustic and hydrosulphite (in the latter case under reduction of the dyestuff), is exposed to air in sunlight or under the Fadeometer (10 minutes at 25 cm. distance). But experiments show that (working with a number of different yellow or orange vat dyestuffs), the amount of oxycellulose formed is much greater in the case of the swatches carrying reduced dyestuff. S. and G. feel that in the case of the reduced vat, the formation of hydrogen peroxide is largely due to auto-oxidation. They find that peroxide is formed and can be detected when a swatch dyed with one of the yellow vats is reduced with hydrosulphite without alkali, carefully washed, and oxidized, all this in the dark. Other work confirming this almost unavoidable formation of

peroxide is quoted also. E.g., Scholefield and Preston detected the formation of peroxide in merely aqueous suspension of yellow or orange dyestuffs (vats), under the influence of light. The authors of the present paper have established further, the following: a distinct formation of oxycellulose takes place when cotton dyed with Cibanone Yellow R or Cibanone Orange R is wetted out with a 0.5% neutral solution of hydrogen peroxide and irradiated, while the same material, so prepared, but wetted out only with water, shows either little or no formation of oxycellulose; also, that mixed dyeings of yellows and blues, e.g., Duranthrene Blue and Anthra Yellow GC, Indanthrene Blue RS and Anthra Yellow GC, Ciba Blue 2B and Anthra Yellow GC, and Indigo and Cibanone Orange R, reduced with acid hydrosulphite, washed, and then exposed wet in the Fadeometer for 15-20 minutes, show distinct degradation of the blue component, while similar dyeings, unreduced but wet, show no alteration in the blues; and further, that a similar series of swatches wetted out with a 0.5% solution of hydrogen peroxide, also suffer degradation in the blues. There seems to be no question that (a) hydrogen peroxide is formed in the oxidation of the yellow vat dyestuffs from the reduced form, and (b) that the peroxide at least increases or hastens the formation of oxycellulose, even if it is not the cause of it. It is an interesting fact that all the dyestuffs found to be active in this way are also fluorescent in ultra-violet light.

Delustering of Artificial Silks

H. Brandenburger—Kunst-Seide 12,102 (1930)—The decreasing of the high luster of artificial silks in the effort to bring its appearance more nearly to that of natural silk, has become a matter of considerable importance. The question has not been much to the fore in Germany up to the present, but is now demanding attention because of the introduction from England of goods of this sort. While the article is intended principally for consumption, in Germany a summary of it may be not without interest here.

There are two general methods pursued, a purely mechanical, and a chemical method. The latter is of use less with viscose than with acetate silk. With viscose, we can treat (E. P. No. 264,529) with strong caustic liquor of about the strength of mercerizing liquor, or with strong solutions of soda, acids, or zinc chloride. Another way (E. P. No. 293,752) consists in drawing the fiber through water, and stretching and strongly twisting it simultaneously. The alteration in appearance is due in this case to superficial alteration of structure while in the swelled condition. In acetate-silk, only the saponification method is used. Acetate-silk is notoriously sensitive toward boiling water and toward even very weak alkali solutions. This sort of superficial saponification was used in the earlier stages of the artificial fiber industry to make the material more receptive toward the ordinary cotton dyestuffs. Now the same process is used, and to a large extent, principally for delustering the fiber whose luster used to be so highly prized. The correct procedure, especially with mixed weaves, is to deluster before the dyeing, since otherwise the characteristic of the acetate-silk, to take up only acetate-silk dyestuffs, is altered in favor of the cotton dyestuffs. Great care has to be taken, not only because the acetate-silk loses tensile strength by careless handling and over-vigorous saponification, but also to attain a perfectly even saponification and consequent uniform delustering.

As to the mechanical method—if we consider the synthesis of fiber already delustered in the spinning-process itself, there are many possible ways to the end desired. Since the luster originates in surface-reflection of light from the fiber, such fibers as have a highly irregular cross-section offer many points of reflection on their surface, and are therefore of high luster. If the conditions of spinning produce a more and more cylindrical fiber, circular in cross-section, such a fiber loses in luster as its cross-section, so to say, smooths out. Cupro-silk characteristically displays a rather dull luster; this is due to the obstinate retention in the fiber of copper compounds too small in amount to be detected analytically, but certainly there in spite of the most careful "de-coppering". This has led to a method of delustering the more highly lustrous fibers by incorporating in them, during the spinning-process, substances which will produce the result commented upon in the case of cupro-silk. Substances which produce cloudiness or turbidity in the spinning-fluid before spinning, or which produce this cloudiness during the actual generation of the fiber, may of course be used. One process (E. P. No. 273,386) adds to the viscose before spinning, high-boiling petroleum fractions up to a maximum of 5%; this solution is best spun in a bath containing zinc salts (D. R.-P. No. 260,479). Another similar patent (E. P. No. 273,647) adds fats, oils, soaps, or hydrogenated hydrocarbons, or in other procedures, fats, waxes, metallic oxides, or metallic soaps. (E. P. No. 294,623) adds barium sulphate or lead sulphate to the acetyl-cellulose solution. Such additions render the spinning-solution turbid before spinning. The other possibility, that of adding to the spinning-solution a substance which will develop the desired cloudiness in the fiber during or after spinning would be exemplified by addition to the solution of a suitable sulphide, which in coming into contact with the fiber in the spinning-bath as it is in the very act of coming into being, would liberate free, finely-divided sulphur. A Dutch firm markets viscose delustered in this way. Unica silk, too, contains a good deal of this free sulphur, whose presence can be recognized by its odor on dyeing. The apprehension that an excessive sulphur content would unfavorably influence the level-dyeing properties of the fiber has not been realized.

Another problem is involved in the need of delustering artificial silk in woven material and in piece-goods. This is usually carried out after dyeing. The method mostly used consists in precipitating upon the fiber such insoluble compounds as produce the effect of delustering without a

smutting of the material. The barium sulphate and the titanium chloride method are the ones most used. The first consists merely in impregnating the goods with barium chloride solution, and then passing them into a precipitating-bath containing soluble sulphates. Sulphuric acid is of course out of the question because of the practical impossibility of washing it out so completely as would be necessary to avoid tendering upon storage. The method is not the best possible, since the degree of delustering desired is not always possible of attainment; the barium sulphate in addition, is mostly deposited upon the surface of the fiber, and gradually washes off with consequent reappearance of the luster, and this perhaps not evenly. The titanium chloride method is similar—impregnation of the fiber with titanium chloride solution, precipitation of titanium hydroxide upon the material by passage through a weakly alkaline bath, and final conversion of the hydroxide to the oxide by suitable drying. In this process, the cost of the titanium compound is not low, to say the least; and besides, careless drying renders the fabric hard and brittle. A third method, hardly used any longer, consisted in roughening the surface of the fabric by coating it with microscopically fine crystals or similar material, as glass powder, or silicates (a kind of textile sand-paper).

Better methods are needed, and are being sought. It is odd to reflect, however, that even a few years ago the chief claim of the artificial silks to public favor consisted in their high luster, as competitors with natural silk, whose luster some artificial fibers boasted of surpassing. The chief claim being advanced now lies rather in the ability of the different kinds of artificial fiber, when woven into patterns, to take up different kinds of dyestuffs, of different tones, from even a single bath, so as to get polychrome effects with (for the dyer, at least) minimum trouble; and the question of high luster in many cases is a disagreeable one. Considering the instability of popular whims, we may before many years, find the old-fashioned plain cotton fabrics, printed or dyed with sober restraint, demanded by the public as a measure of protection against the gaiety of the present artificial-silk products.

Nitrogen in Cotton and Linen

Prof. M. M. Tschilikin—Mell. Textil-Ber. 10,883 (1929)—Prof. Tschilikin's work upon this subject has already been mentioned incidentally in these columns, in connection with the subject of the chloramines as produced in bleaching with hypochlorite—the problem of yellowing. The nitrogen occurs in the natural material in the form of proteins which are not removed by the immersion of the material for 7-8 minutes in a sour of ¾° Bé. sulphuric acid. Diastaphor has little effect upon these proteins. Alkaline kier-boiling dissolves and removes them, in which process T. finds that some ammonia is evolved, pointing to actual breaking down of the proteins, apart from their mere removal. But a part of the protein matter adheres obstinately, and is removed completely only by treatment with hypochlorite.

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